KINETICS OF OXIDATION OF SOME NITROGEN AND SULFUR COMPOUNDS

ABSTRACT

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DEPARTMENT OF CHEMISTRY
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A THESIS SUBMITTED
IN
FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF
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To

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1. KINETICS OF OXIDATION OF SOME ALIPHATIC AMINES BY ALKALINE HEXACYANOFERRATE (III)

The kinetics of oxidation of some aliphatic amines (methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of these reactions were found to be dependent on the first powers of the concentra tions of both, substrate and oxidant. The rate of the reaction was independent of the concentration of alkali in the range studied, for methylamine and dimethylamine. An alkaline pH was necessary for the facile oxidation of these amines. Though there was no dependence on [alkali] over the pH range studied, the reaction was not independent of pH, in the wider sense.

All the other amines (trimethylamine, ethylamine, diethylamine and triethylamine) underwent facile oxidation by aqueous hexacyanoferrate (III) in neutral medium, that is, without using any alkali.

The effect of changes in temperature on the rates of the reactions has been studied, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium,

changes in the concentrations of added hexacyanoferrate (II) ions, and the addition of salts, did not have any effect on the rates of these reactions.

The presence of radical intermediates, formed in the rate determining step of the reaction, has been detected and characterized by ESR spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of radical intermediates in the rate determining step. The radical underwent further reaction to yield the products. The products formed from the oxidation of methylamine, dimethylamine and trimethylamine were the respective N-acyl derivatives. The products from the oxidation of ethylamine, diethylamine and triethylamine, were the respective dealkylated products. These products were characterized by analytical and spectral methods.

2. KINETICS OF OXIDATION OF SOME AROMATIC AMINES BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of some aromatic amines (aniline and substituted anilines, N-methylaniline, N-ethylaniline, N,N-dimethylaniline, N,N-diethylaniline, benzylamine and substituted benzylamines, diphenylamine and substituted diphenylamines) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen

atmosphere has been studied.

The rates of these reactions were dependent on the first powers of the concentrations of both, substrate and oxidant. The rate of the reaction was independent of the concentration of alkali in the range studied. An alkaline pH was necessary for the facile oxidation of these amines.

The reactions were influenced by changes in the temperature, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, and the addition of salts, did not have any effect on the rates of these reactions.

Increasing proportions of methanol resulted in an increase in the rate of oxidation, in the case of aniline and diphenylamine. In the case of N,N-dimethylaniline, the reverse trend was observed. Plots of log k_{obs} against the reciprocal of the dielectric constant were linear, indicating that the reactions under consideration were of the ion-dipole type.

The introduction of electron-releasing groups caused an increase in the rate of the reaction, whereas electron-withdrawing groups caused a decrease in the rate of the reaction. Hammett plots of log k_{obs} against σ^+ (or σ^-) were linear, with the values of $\rho^+ = -1.0$ (anilines), and $\rho = -1.0$ (for diphenylamines and benzylamines). The ρ values for these substrates (anilines, diphenylamines and

benzylamines) were in the range for processes wherein the rate determining step involved the formation of radical intermediates.

The oxidation of benzylamine -α-d_2 exhibited a kinetic isotope effect, with k_H/k_D = 6.3, indicating a cleavage of the C-H bond of the methylene group attached to the aryl ring, resulting in the formation of a radical intermediate in the rate - determining step of the reaction.

The presence of radical intermediates was detected and characterized by ESR spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of a radical intermediate in the rate determining step. The radical was rapidly converted to the products. Efforts to isolate intermediate product(s) were not successful.

The products obtained from the oxidation of the various aromatic amines, were:

(a) azobenzene (80-85%), from the oxidation of aniline;

(b) formanilide (70%) from the oxidation of N-methylaniline;

(c) formanilide (70%) and formaldehyde (10%), from the oxidation of N-ethylaniline;

(d) N-methylformanilide (75%), from the oxidation of N,N-dimethylaniline;

(e) formanilide (70%), acetaldehyde (10%) and formaldehyde (10%),

from the oxidation of N,N-diethylaniline;

(f) tetraphenylhydrazine (80%), from the oxidation of diphenylamine;

(g) benzaldehyde (80%) and ammonia, from the oxidation of benzylamine.

The products formed, in each case, were isolated and characterized by analytical and spectral methods.

3. KINETICS OF OXIDATION OF SOME INORGANIC SULFUR COMPOUNDS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of some inorganic sulfur compounds (sulfite, metabisulfite, dithionite, thiosulfate and thiocyanate) by potassium hexacyanoferrate(III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of the reactions were observed to be dependent on the first powers of the concentrations of each, substrate and oxidant. The rates of the reactions were dependent on the first powers of the concentrations of alkali in the range studied, in the case of sulfite, metabisulfite and dithionite ions. In the case of thiosulfate and thiocyanate ions, the rates were independent of the concentrations of alkali in the range studied.

The rates of the reactions were influenced by changes in temperature, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium, and changes in the concentrations of added hexacyanoferrate (II) ions, did not have any effect on the rates of these reactions.

Radical intermediates were detected in the oxidation reactions of sulfite, dithionite and thiocyanate ions.

The mechanistic pathway envisaged the formation of radical intermediates, in the case of the oxidation of sulfite, dithionite and thiocyanate ions. Rapid dimerization yielded the products, which were isolated and characterized. In the oxidation of thiosulfate, the intermediate anion underwent rapid dimerization to yield the product, which was isolated and characterized.

4. KINETICS OF OXIDATION OF SOME ORGANIC SULFUR COMPOUNDS BY ACIDIC HEXACYANOFERRATE (III).

The kinetics of oxidation of some organic sulfur compounds (thiomalic acid, thioglycolic acid and thiophenol) by potassium hexacyanoferrate (III), in acidic medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of the reactions showed a first order dependence on the concentrations of each, substrate and oxidant. The rates of the reactions showed a first order dependence on the concentration of acid (in the case of thioglycolic acid and thiophenol), but showed an inverse dependence on the concentration of the acid, in the case of thiomalic acid.

The rates of the reactions were enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

Increasing proportions of methanol resulted in an increase in the rate of the reaction, in the case of thiophenol. A plot of log k_{obs} against the reciprocal of the dielectric constant was linear, indicating that the reaction was of the ion-dipole type.

Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, the addition of salts, and the addition of the product itself, did not have any effect on the rates of these oxidation reactions.

The presence of radical intermediates was detected and characterized by ESR spectroscopy.

The mechanism of the reaction involved the formation

of radical intermediates in the rate determining step. The subsequent step involved a rapid dimerization of the radical, to yield the respective disulfide. The products formed have been characterized by analytical and spectral methods.

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I certify that the thesis entitled "KINETICS OF OXIDATION OF SOME NITROGEN AND SULPHUR COMPOUNDS" submitted by **Miss Gopa Dasgupta** for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by her under my supervision. She has been duly registered, and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

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C O N T E N T S

1

INTRODUCTION

Metal ion oxidants can function either as one-equivalent or two-equivalent reagents. One-equivalent oxidants are those which accept a single electron by direct transfer or by interaction with a hydrogen atom. Two-equivelent oxidants can accept two electrons from the substrate.

In one-equivalent redox processes, the change of valency can be brought about by either an inner-sphere or an outer-sphere mechanism(1).

1. Inner-sphere mechanism:

The inner-sphere or bonded mechanism envisages a direct contact between the oxidant and the reductant, and the transition state is characterised by a ligand which is bonded to both metal ions. It can therefore act as a bridge between them for the transfer of an electron. The typical reaction is (2):

$$Cr^{2+}aq + (NH_3)_5\ Co^{III}\ Cl^{2+} \longrightarrow$$

$$CrCl^{2+}\ aq + Co^{2+}\ aq + 5\ NH_3$$

The formation of an inner-sphere transition state would lead to considerable distortion of the ions, which may thus assist electron transfer by reducing the energy terms involved. In order that an inner-sphere mechanism can operate,

the ligand present should behave in a bidentate manner. The ligand must possess available pi-orbitals, and one of the reagents involved must have a ligand which can be easily displaced.

2. Outer-sphere mechanism:

Outer-sphere electron exchange reactions constitute the simplest class of electron transfer reactions. In an outer-sphere mechanism, the inner co-ordination shell of both reagents is preserved intact in the transition state. Since the metal-ligand distances will be affected by valency change, some distortion of the inner shells would occur, but no metal-ligand bond would be broken or formed.

The criteria for outer-sphere or non-bonded reactions are as follows:

(a) there must be no observed transfer of ligands between the reagents;

(b) the rate of the reaction may have any magnitude, but if it is faster than any reasonable rate of substitution of the ligands of either oxidant or reductant, then the reaction can be classified as an outer sphere reaction;

(c) the activation energy of this type of reaction should be much less than that anticipated for a mechanism involving ligand - metal bond fission;

(d) the kinetic law of the reaction must show that the transition state has the same composition as the sum of the reagent molecules.

It would therefore be expected that most outer sphere processes would be fast reactions between complexes which are substitution-inert, in solvents which are not themselves providing ligands.

Most organic reaction processes are explicable in terms of electron shifts accompanying bond formation and bond breaking. The rates and activation energies of such reactions are therefore of considerable interest.

The essential steps in these reactions would be:

(a) the approach of two reagent ions, which may be aided or hindered by electrostatic forces;

(b) before electron transfer can occur, two conditions must be obeyed (3), in accordance with the Franck-Condon principle:

(i) the electron transfer must not alter the energy of the system. This electron transfer occurs in a very short time, and the only possible loss or gain of energy would be by radiation. Electron transfer can occur only if the oxidant and reductant have been vibrationally excited to the same total energy. Thus, when the two valency states of a reagent are closely similar in bond energy and geometry, the outer-sphere process would be expected to be most facile.

(ii) the overall spin angular momentum should not be altered.

(c) the process of electron transfer itself. If the reagent complexes are sufficiently close and of suitable symmetry, such that there is some interaction between the orbitals involved in electron transfer, then the probability of electron transfer would be essentially unity. The requirement of orbital overlap can be related to the orbitals of the reagents. This would suggest that in octahedral complexes, t_{2g} electrons might be more easily transferred than e_g electrons which are in orbitals directed along the metal-ligand axis.

In order to establish that an outer-sphere or non-bonded electron transfer can occur from an organic compound to a metal oxidant, it is necessary to choose a suitable model system in which the probability of non-bonded mechanism would be a maximum, and that of the competing bonded process a minimum. The oxidant should be so chosen such that it possesses ligands which are slow or difficult to replace. The organic substrate should be so chosen such that it is not likely to displace ligands from a metal ion complex. Examples of such exchange-inert oxidants are the iron (III) tris-o-phenanthroline complex (4), $IrCl_6^{2-}$ ion (5), Mn (III) tris-acetylacetone complex (6), ceric ions (7), and the hexacyanoferrate (III) ion (8,9).

In the reactions of one-equivalent oxidants with organic substrates, the most frequently encountered oxidation process would seem to correspond to an electron transfer between substrate and oxidant, accompanied by the breaking of a C-H bond and loss of a proton to give a substrate radical as for example (1C):

$$Co\ (III) + C_6H_5CH_3 \longrightarrow Co\ (II) + C_6H_5\dot{C}H_2 + H^+ \quad .$$

It would therefore be expected that the loss of a proton would be slower than electron transfer, and hence would correspond to the rate determining step.

The presence of radicals may be inferred by their oxidation or reduction of added inorganic ions, or by their ability to cause polymerisation to occur with added monomer, as for example, acrylamide or acrylonitrile. If the radical is present in sufficiently high concentrations, its presence can be detected by electron spin resonance spectroscopy.

Although the radical may undergo many other processes, it is most probable that in the presence of an excess of oxidant, the radical will be oxidised further. Examples are known where the main mechanisms of this step may be: (a) a non-bonded electron transfer (conversion of a neutral radical to a cation), as for example the oxidation of 2,6-dimethylphenol by hexachloroiridate ion (5), and the oxidation of hydroquinones by ferric ions (11); (b) bonded electron transfer

or the transfer of a ligand from the oxidant to the radical, as for example, the reduction of $IrCl_6^{2-}$ by Cr^{2+} ions(12); (c) redox substitution, in which the radical remains attached to the complex, as for example, the phenylation of the ferricenium complex (13,14); (d) redox addition, where the radical remains attached to the complex, as for example, the reaction of hexacyanoferrate (III) with isobutyraldehyde(15).

Oxidation of organic substrates with potassium hexacyanoferrate (III).

Potassium hexacyanoferrate (III), $K_3Fe(CN)_6$, is essentially a substitution-inert transition metal complex (16). It does not exchange its ligands at a rate fast enough to complete with rapid electron transfer. Therefore, oxidations by hexacyanoferrate (III) ion occur by means of a non-bonded electron transfer or outer sphere process, whereby an electron is transferred from the substrate to the metal ion through the cyano ligand.

In acidic medium, potassium hexacyanoferrate (III) has been used for the oxidation of sulfur containing compounds (17-25), toluene and substituted toluenes (26-29), diphenylmethane and triphenylmethane (30), fluorene (31), unsaturated systems (32-33), and polynuclear systems (34,35).

In alkaline medium, potassium hexacyanoferrate(III) has been extensively used for the oxidation of various kinds of organic substrates such as aldehydes (36-40), ketones (36,37,41-47), alcohols and diols (48-61), sulfur compounds (62-69), acids (70-81), sugars (82-85), hydrazines (86-89), acyloins (90-92), As (III) 93-95, hypophosphite (96,97), hydrocarbons (98), phenols (99-116), amino acids (117-119), amines (120-127), and the 10-methylacridinium cation (128).

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SCOPE OF THE

PRESENT INVESTIGATION

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The present investigation is a detailed kinetic probe into the oxidation of various organic and inorganic substrates by potassium hexacyanoferrate (III) in alkaline medium, at constant ionic strength, in aqueous methanol, under a nitrogen atmosphere. The organic sulfur compounds have been oxidized by potassium hexacyanoferrate (III) in acidic medium.

The purpose of this kinetic investigation has been to attempt to extend the scope of this extremely efficient and versatile one-electron oxidizing agent, potassium hexacyanoferrate (III), in alkaline and acidic media, and to explore and establish mechanistic pathways of reactions involving the oxidation of nitrogen and sulfur compounds.

The purpose of the present study was:

(1) to study the kinetic features of the oxidation of nitrogen and sulfur compounds;

(2) to demonstrate the usefulness of potassium hexacyanoferrate (III) as a reagent which can bring about the following kinds of reactions;

   (a) oxidative dealkylation of aliphatic amines;

   (b) oxidative coupling of aromatic amines;

   (c) Oxidation of N-alkyl side chains of aromatic amines.

In the present investigation, the substrates chosen for the purposes of oxidation by potassium hexacyanoferrate (III), in alkaline medium, have included:

1. Aliphatic amines (methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine)
2. Aromatic amines (aniline and substituted anilines,, benzylamine and substituted benzylamines, diphenylamine and substituted diphenylamines, N-methylaniline, N-ethylaniline, N,N-dimethylaniline, N,N-diethylaniline).
3. Inorganic sulfur compounds (sulfite, metabisulfite, dithionite, thiosulfate and thiocyanate)
4. Organic sulfur compounds (thiomalic acid, thioglycolic acid, thiophenol). The oxidation of organic sulfur compounds has been carried out in acidic medium.

All the reactions have been carried out under nitrogen atmosphere, so as to ensure the absence of any aerial oxidation.

For each oxidation reaction, the stoichiometry of the reaction has been determined. The concentrations of the substrate, oxidant and alkali (or acid) have been varied, and the effects of these variations on the reaction rates have been studied. The solvent composition has been varied, in order to study the effect of dielectric constant

on the rate of the reaction. Changes in the temperature of the reaction medium have been made, and the activation parameters were evaluated. Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, the addition of salts, and the effect of added product on the rates of the reactions have been studied. The presence of radical intermediates has been detected and characterized by ESR spectroscopy. For each reaction, the products have been isolated and characterized by analytical and spectral methods. The mechanistic pathway for each reaction has been suggested, and the presence of radical intermediates has been confirmed by ESR spectroscopy, polymerization reactions, the Hammett plots and kinetic isotope effects.

PURIFICATION OF MATERIALS AND PREPARATION OF COMPOUNDS

Conductivity Water:

Conductivity water was prepared by the following method: tap water was distilled first with alkaline potassium permanganate and then redistilled with Merck "Pro Analysi" sulphuric acid from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel (Sunvic, U.K.). The conductivity water thus prepared was utilised for the preparation of all the solutions used in the kinetic determinations.

Methanol:

Methanol (E.Merck) was distilled before use (bp 65°C).

Sodium hydroxide:

E. Merck sample was used.

Potassium hexacyanoferrate (III):

E. Merck sample was used.

Potassium hexacyanoferrate (II).

E. Merck sample was used.

Potassium Chloride

BDH (AR) grade sample was used.

Sodium perchlorate:

Sodium perchlorate was prepared by neutralising 70% perchloric acid (E. Merck) with sodium hydroxide (E.Merck). The solution was concentrated, when crystals of sodium perchlorate were obtained. The crystals were filtered, and recrystallised from water. The recrystallised product was dried over silica gel under vacuum. This sample of sodium perchlorate was used for the preparation of stock solutions which were employed for maintaining the ionic strength of the medium.

Substrates

Methylamine (30%, w/v), dimethylamine (40%,w/v) and trimethylamine (30%, w/v) were SD's samples. Ethylamine (40%, w/v), diethylamine and triethylamine were SD's samples.

Aniline and the substituted anilines, N-methylaniline, N-ethylaniline, N,N-dimethylaniline, N,N-diethylaniline, benzylamine and the substituted benzylamines, diphenylamine and the substituted diphenylamines were all E. Merck samples. Thiomalic acid was an SD's sample. Thioglycolic acid and thiophenol were E. Merck samples. Sodium sulfite, sodium thiosulfate and sodium thiocyanate were SD's samples. Sodium dithionite and potassium metabisulfite were obtained from Loba Chemical Co..

All the substrates were purified by distillation or crystallization until their boiling points or melting points, respectively were in agreement with literature values. The purity of each of the substrates was checked by spectral analysis.

All ir spectra were recorded on an IR-297 (Perkin Elmer) spectrophotometer, uv spectra on an UV-26 (Beckman) spectrophotometer, nmr spectra on an EM-390 (Varian) 90 MHz NMR spectrometer, and esr spectra on an E-4 (Varian) EPR spectrometer.

The boiling points, melting points and the spectral data obtained for each of the substrates used, are summarised in Table 1.

TABLE 1

Substrate	Boiling points or Melting Points(^{o}C)	uv(nm)*
(1)	(2)	(3)
Methylamine	30%, w/v	190 (M)
Dimethylamine	40%, w/v	188 (M)
Trimethylamine	30%, w/v	192 (M)
Ethylamine	40%, w/v	177 (M)
Diethylamine	56 (bp)	194 (M)
Triethylamine	89 (bp)	196 (M)

(1)	(2)	(3)
Aniline	184 (bp)	230 (H)
p-anisidine	57 (mp)	232 (cH)
o-anisidine	225 (bp)	237 (cH)
p-toluidine	42 (mp)	236 (M)
o-toluidine	200 (bp)	233 (M)
m-toluidine	203 (bp)	238 (M)
p-chloroaniline	232 (bp)	296 (M)
o-chloroaniline	208 (bp)	290 (cH)
m-chloroaniline	230 (bp)	292 (E)
p-nitroaniline	148 (mp)	228 (A)
o-nitroaniline	72 (mp)	231 (A)
m-nitroaniline	114 (mp)	235 (A)
Benzylamine	185 (bp)	265 (iO)
p-methoxybenzylamine	236(bp)	254 (M)
p-methylbenzylamine	204(bp)	270 (M)
m-methylbenzylamine	206 (bp)	250 (M)
m-methoxybenzylamine	141 (bp)	245 (M)
p-chlorobenzylamine	109 (bp)	291 (M)
m-chlprobenzylamine	89 (bp)	288 (M)
p-nitrobenzylamine	40 (mp)	275 (M)
m-nitrobenzylamine	65 (mp)	260 (M)
Diphenylamine	54 (mp)	208 (M)
p-aminodiphenylamine	66 (mp)	286 (M)

(1)	(2)	(3)
p-methoxydiphenylamine	105 (mp)	284 (A)
p-methyldiphenylamine	293 (bp)	206 (A)
m-nitrodiphenylamine	114 (mp)	265 (A)
p-nitrodiphenylamine	133 (mp)	258 (M)
N-methylaniline	196 (bp)	293 (M)
N-ethylaniline	205 (bp)	295 (M)
N,N-dimethylaniline	194 (bp)	205 (A)
N,N-diethylaniline	216 (bp)	258 (M)
Sodium Sulfite	150 (mp)	-
Sodium thiosulfate	48 (mp)	-
Sodium thiocyanate	287 (mp)	-
Sodium dithionite	52 (mp)	-
Potassium metabisulfite	190 (mp)	-
Thiomalic acid	154 (mp)	228 (A)
Thioglycolic acid	120 (bp)	240 (cH)
Thiophenol	169 (bp)	236 (cH)

* A = Alcohol;
  M = Methanol;
  H = Hexane;
  iO = Isooctane
  cH = cyclohexane

Kinetic method:

All the standard flasks and reaction vessels were of pyrex glass with well-ground stoppers. The reaction vessels used were stoppered conical flasks which were painted black on the outside to prevent any photochemical change. All the glass apparatus used were tested for loss of solvent, and the loss was found to be negligible. The standard flasks, reaction vessels and the pipettes used were standardised, using conductivity water, and the correction was found out and applied.

An electrically operated thermostatic water-bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers with proper cooling arrangements for continuous work. A xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperatures accurately, with fluctuations of not more than $\pm$ 0.1^{o}C. The temperatures were recorded by means of an accurate sensitive thermometer, reading to tenths of a degree. The bath-liquid was water, covered with a layer of liquid paraffin to minimise evaporation of water and loss of heat due to radiation.

Spectrophotometers:

For absorption measurements, the spectrophotometers used were (a) Digital spectrophotometer type 106, MK II model

(systronics), and (b) UV-26 (Beckman) UV-Visible spectrophotometer.

(a) The MK II model (Systronics) spectrophotometer was a single beam spectrophotometer having a grating of 600 lines/mm, and a wavelength range from 340 nm to 960 nm. The nominal spectral slit width was 20 nm, constant over the entire range. The full scale deflection could be obtained over the wavelength range of 340 nm to 600 nm. By the addition of a red filter and interchanging of the phototube, the range could be extended to 960 nm. In order to ensure maximum sensitivity of the instrument, and to minimise the errors in measurements of optical density due to fluctuations in voltage, the spectrophotometer was connected to the mains through an external voltage-stabiliser. This was in addition to the in-built voltage-stabiliser within the instrument itself. The light source was a 15 watt tungsten lamp operated by a regulated power supply. The instrument was calibrated as specified in the instruction manual, over the range of concentrations of K_2CrO_4 in KOH solutions, so as to verify Beer's law at 370 nm.

(b) The UV-26 (Beckman) UV-Visible spectrophotometer was a single monochromator, having a filter-grating of 1200 lines/mm, and a wavelength range from 190 to 900 nm. This spectrophotometer had a thermostatic control arrangement and the

absorbance value was displayed directly on the digital display and on the recorder. Photometric linearity was checked over the range of concentrations of K_2CrO_4 in KOH solutions, as specified in the instruction manual, so as to verify Beer's law at 370 nm.

Absorption cells:

The absorption cells were of 'Corning' glass and of 8 ml capacity for the spectrophotometer 106 MK II model (Systronics). Quartz cells of 5 ml capacity were used for spectral determinations with the UV-26 spectrophotometer (Beckman). All the cells used were thoroughly cleaned by aqueous ethanol and acetone, and dried before they were used for the spectral measurements. After the transfer of the solution to the cell, care was taken to see that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

Solutions of hexacyanoferrate (III) in methanol - water mixtures (60-40 to 75-25% v/v) were prepared. The absorbance of each of these solutions was scanned over the range of wavelengths from 350 nm to 700 nm. The maximum absorption in each case was located at 420 nm (Fig.1). At this wavelength of 420 nm, the absorption due to $Fe(CN)_6^{3-}$ has been observed to be a maximum (1), the absorption due to $Fe(CN)_6^{4-}$ being negligible (2).

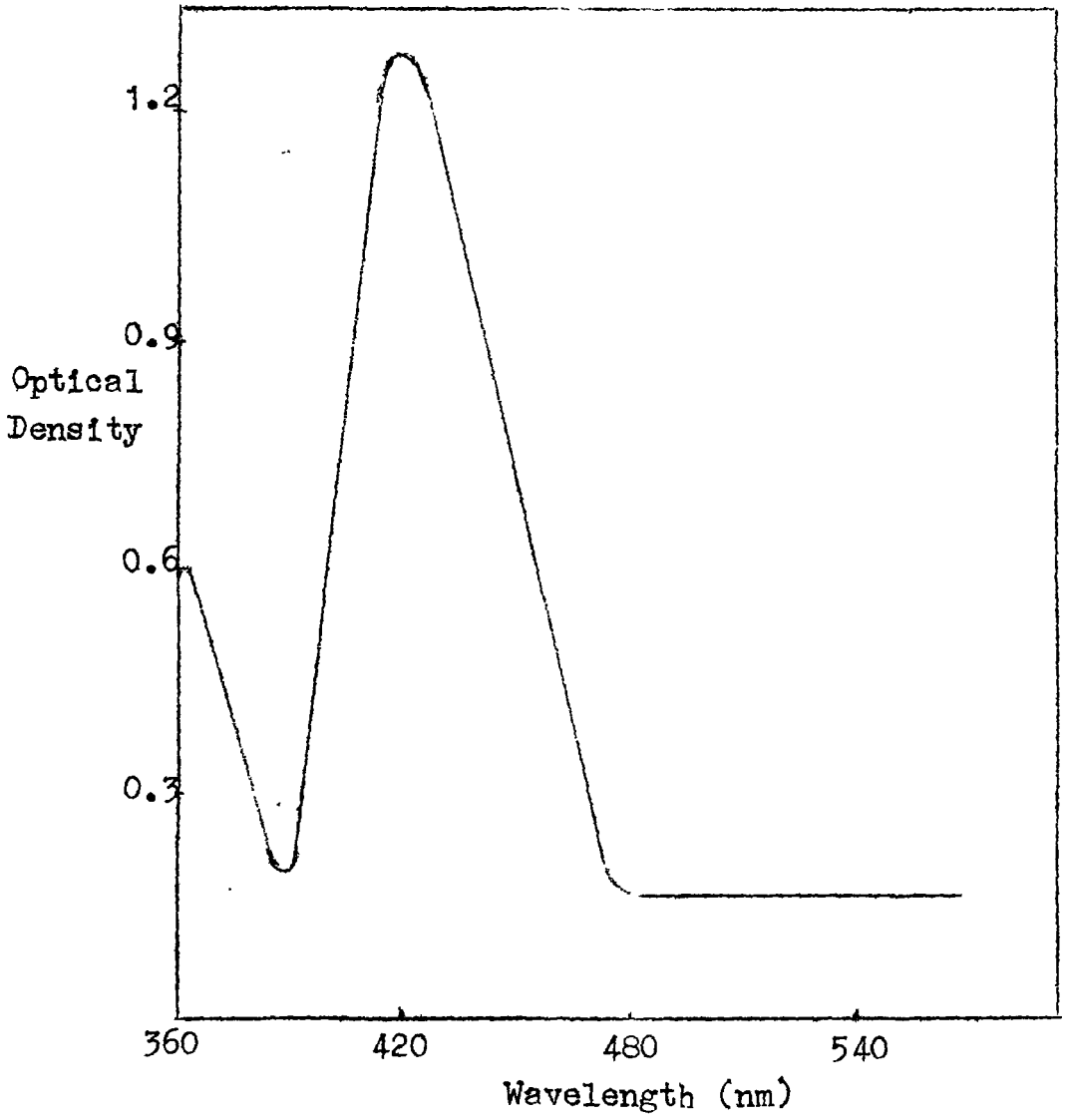

Fig. 1 Plot of absorbance against wavelength (nm) of Potassium Hexacyanoferrate(III).

(Determination of maximum absorption)

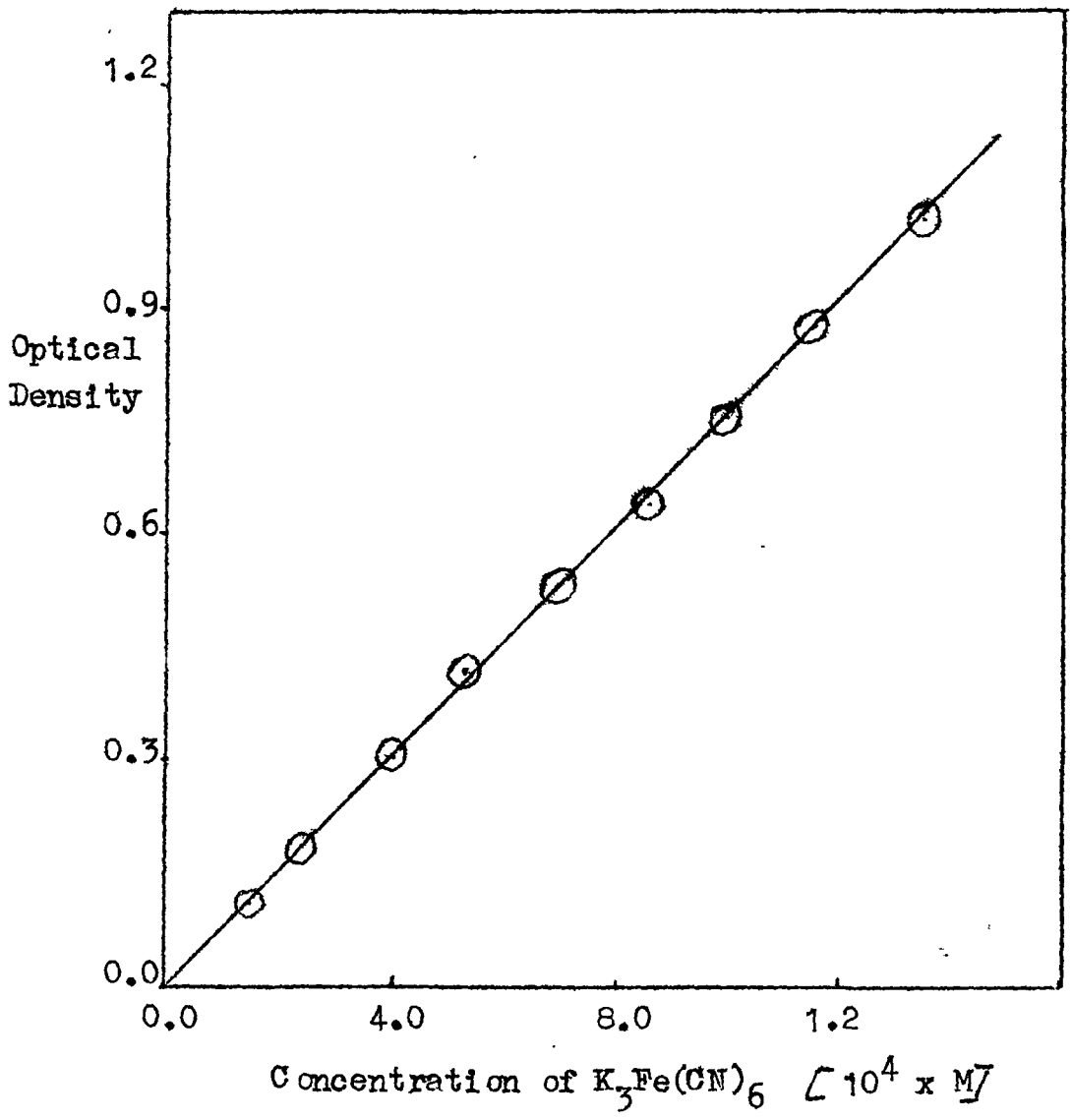

Fig. 2 Verification of Beer-Lambert's Law. Plot of concentration against optical density at 420nm .

At 420 nm, Beer's law was obeyed over the range of concentrations of solutions used. A typical graph of the optical density against the concentration of $Fe(CN)_6^{3-}$ is shown (Fig.2).

In this investigation, all the optical density measurements were carried out at a wavelength of 420 nm.

Rate measurements

A known amount of the substrate was weighed accurately into a 10 ml standard flask and made up with the requisite quantities of methanol and water, so as to make the required molar solution. Potassium hexacyanoferrate (III) was accurately weighed out into a 10 ml standard flask and dissolved in a small volume of water. The requisite amount of sodium hydroxide solution, whose strength had been determined was added to maintain the required alkalinity. Sodium perchlorate (or potassium chloride) was added so as to maintain a constant ionic strength of the medium. The solution was then made up in methanol and water. Sufficient time was allowed to compensate for any change of heat during dilution. The two reactant solutions were separately thermostated at the required temperature for 3 hours, under a nitrogen atmosphere. The solutions were then mixed in equal volumes. The reaction mixture was homogeneous throughout the duration of the reaction.

The progress of the reaction was followed by observing the disappearance of hexacyanoferrate (III). Readings were taken at regular intervals of time, by noting the decrease in optical density at 420 nm, spectrophotometrically.

All the kinetic experiments were carried out in duplicate or in triplicate, and the rate constants which were determined were found to be reproducible to within ±3%.

Calculations:

(a) Rate constants:

For all the kinetic determinations, pseudo-first order reaction conditions have been used, wherein the concentration of the substrate has been taken in a very large excess over that of the concentration of the oxidant.

The pseudo-first order rate constant, k_{obs}, expressed as sec^{-1}, were calculated from the equation (3):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \quad \ldots\ldots \quad (1)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time, t.

The logarithmic plots of optical densities against time were linear, and extrapolation to zero time gave the values of D_o.

The values of the second order rate constant, k_2 , expressed in $M^{-1}\ s^{-1}$, were computed by dividing the pseudo-first order rate constant (k_{obs}, s^{-1}) by the concentration of the substrate (M).

All values of rate constants were the average of two or more experiments, with agreement being within $\pm 3\%$.

(b) Thermodynamic activation parameters:

These parameters were determined from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows:

(i) Activation energy (E)

From the linear plot of log k_{obs} against the reciprocal of temperature (T),

$$\text{slope} = - \frac{E}{2.303\ R}$$

$$E = - \text{slope} \times 2.303\ R \ (\text{kJ mol}^{-1})$$

(ii) Frequency factor (A)

$$k_{obs} = A\ e^{-E/RT}$$

$$\log A = \log k_{obs} + \frac{E}{2.303\ RT}$$

(iii) Enthalpy of Activation ($\triangle H^{\neq}$)

$$\triangle H^{\neq} = E - RT$$

(iv) Entropy of Activation ($\Delta S^{\neq}$)

$$k_{obs} = \frac{kT}{h} e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT}$$

$$\Delta S^{\neq} = 2.303\ R \left[\log k_{obs} + \frac{\Delta H^{\neq}}{2.303\ RT} - \log \frac{kT}{h} \right]$$

where k is the Boltzmann constant, and h is the Planck's constant.

Stoichiometry:

Reaction mixtures containing the substrate and an excess of hexacyanoferrate (III), taken in a known solvent composition of methanol and water, containing the requisite amounts of sodium hydroxide and sodium perchlorate, were allowed to react to completion at a particular temperature. The hexacyanoferrate (III) which was left, was analysed spectrophotometrically at 420 nm. The individual stoichiometric equations are shown along with the reactions of each of the substrates with the oxidant.

Product Analysis

(1) Products obtained from the oxidation of methylamine and dimethylamine

Stoichiometric amounts of substrate and oxidant solutions, taken in 0.1M NaOH (ionic strength adjusted to 0.5 M by the addition of $NaClO_4$), were mixed and heated for 3h at 60°C. The reaction mixture was cooled, extracted with ether, dried over anhydrous $MgSO_4$ and then concentrated.

(i) Product from the oxidation of methylamine

Spotting on TLC plates, using benzene as developer, gave a single spot. The product obtained was formamide (bp 210°C, yield ~ 75-80%). This product was characterized by IR analysis (IR-297, Perkin Elmer), which gave peaks at 3400, 2900, 1700, 1600, 1400, 1320 and 1050 cm^{-1}). NMR analysis (EM-390, 90MHz, Varian) in acetone, gave peaks at 7.0 τ and 8.0 τ.

(ii) Product from the oxidation of dimethylamine

Spotting on TLC plates, using benzene as the developer, gave a single spot. The product obtained was formylmethylamine (bp 182°C, yield ~75%). This product was characterized by IR analysis (IR-297, Perkin Elmer), which gave peaks at 3300, 3030, 2860, 1670, 1540, 1390, 1250, 1150 and 960 cm^{-1}.

(2) Product obtained from the oxidation of trimethylamine

Stoichiometric amounts of the substrate (1 mol) and oxidant (4 mol) solutions were mixed and heated for 3h at 60°C. The reaction mixture was cooled, extracted with ether, concentrated and dried over anhydrous $MgSO_4$, to give the product, formyldimethylamine (yield ~ 75%). This product was characterized by bp(154°C) and by IR analysis (IR-297, Perkin Elmer), which gave peaks at 2940, 1670, 1490, 1430, 1390, 1250 and 1090 cm^{-1}.

(3) Products obtained from the oxidation of ethylamine

Solutions of substrate ($5x10^{-2}M$) and oxidant ($5x10^{-3}M$) were mixed and kept at 35°C for 24h, under nitrogen. The evolution of ammonia was detected by the Nessler's reagent test (4 a).

5 ml of the reaction mixture, possessing an acetaldehyde odour, was mixed with 10 ml of 0.4% dimedone solution buffered to pH 5.0 with 0.2 M acetate. Within a few minutes, a precipitate of the dimedone derivative of acetaldehyde was formed. This derivative was recrystallized from ethanol (yield ~ 75%; mp. 141°C; lit. value, 140°C , ref.5). This derivative was converted to the anhydride by boiling it (0.2g) for 3h in a mixture of 7 ml ethanol and 10 ml of 1N HCl, and later diluting with 20 ml of water (mp 175°C, lit. value, 175-176°C).

(4) Products obtained from the oxidation of diethylamine

Solutions of substrate (5×10^{-2} M) and oxidant ($5x10^{-3}$ M) were mixed and kept at 35°C for 24h under nitrogen. The reaction mixture, possessing an acetaldehyde odour, was divided into 3 parts:

(i) 5 ml of the reaction mixture was mixed with 10 ml of 0.4% dimedone solution buffered to pH 5.0 with 0.2 M acetate. A precipitate of the dimedone derivative of acetaldehyde was formed. This derivative was recrystallized

from ethanol (yield ~ 75%; mp 141°C, lit. value 140°C). This derivative was converted to the anhydride by boiling it (0.2g) for 3h in a mixture of 7 ml ethanol and 10 ml of 1N HCl, and later diluting with 20 ml water (mp 175°C, lit. value, 175-176°C).

(ii) the picrate derivative of ethylamine was prepared, and recrystallized from methanol as yellow prisms (mp 165°C).

(iii) 5 ml of the reaction mixture was acidified with 2 ml of 2N HCl, and then evaporated at reduced pressure to a white solid, smelling faintly of acetaldehyde. The solid was distilled from 50% NaOH (10 ml) into ether, and evaporated at reduced pressure to a white solid residue, ethylamine hydrochloride (mp 227°C). The IR spectrum (IR-297, Perkin Elmer) of this sample was identical with that of ethylamine hydrochloride (6 a).

(5) Products obtained from the oxidation of triethylamine

Solutions of substrate ($5x10^{-2}$M) and Oxidant ($5x10^{-3}$M) were mixed and kept at 35°C for 24h, under nitrogen. The reaction mixture, possessing an acetaldehyde odour, was divided into 3 parts:

(i) 2 ml of the reaction mixture was mixed with 5 ml of cold water. This solution, on testing for acetaldehyde by the p-phenylphenol-sulfuric acid test (7), exhibited a strong positive reaction, not obtained with a triethylamine blank.

(ii) 2 ml of the reaction mixture was mixed with 5 ml of 0.4% dimedone solution buffered to pH 5.0 with 0.2M acetate. A precipitate of the dimedone derivative of acetaldehyde was formed, which was recrystallized from ethanol (yield ~ 75%; mp 141°C, lit. value, 140°C). This derivative was converted to the anhydride by boiling it (0.2g) for 3h in a mixture of 7 ml ethanol and 10 ml of 1N HCl, and later diluting with 20 ml water (mp 175°C, lit. value, 175-176°C).

(iii) 5 ml of the reaction mixture was acidified with 2 ml of 2N HCl, and then evaporated at reduced pressure to a white solid, smelling faintly of acetaldehyde. The solid was distilled from 50% NaOH (10 ml) into ether, and evaporated at reduced pressure to a white solid residue, diethylamine hydrochloride (mp 227°C). The IR spectrum (IR-297, Perkin Elmer) of this sample was identical with that of diethylamine hydrochloride (6b).

(6) Product obtained from the oxidation of aniline

Stoichiometric amounts of substrate and oxidant, dissolved in aqueous methanol (30%, v/v), containing NaOH (0.025M) and the ionic strength adjusted to 0.3M by the addition of $NaClO_4$, were mixed and kept at 35°C for 24h, under nitrogen. The solvent was removed, and the residue extracted

with hot benzene. The cooled benzene extract was filtered, concentrated, and chromatographed on alumina, using benzene for elution. The product, obtained in about 80-85% yield as orange red crystals, was identified and characterized as azobenzene (mp 68°C; IR bands at 1590, 1490, 1460, 1300, 1220, 1160, 1080, 1020, 930 and 750 cm^{-1}).

(7) Product obtained from the oxidation of N-methylaniline

Solutions of the substrate ($1x10^{-2}$M) and oxidant ($1x10^{-3}$M), taken in aqueous methanol (60%, v/v) containing NaOH(0.01 M) and KCl(ionic strength adjusted to 0.1M), were mixed and kept at 35°C for 24h, under nitrogen. The solvent was removed, the residue was washed with dilute HCl, and then concentrated. The crude product obtained was distilled under pressure. The distillate was crystallized from a 1:1 mixture of toluene and petroleum ether at 0°C to give the product, formanilide (yield ~70%, mp 50°C). The product was identified by IR analysis (6c), and by NMR analysis in CCl_4, which gave peaks at 6.8 δ (aromatic protons), 3.8 δ (N-H proton) and 9.5 δ (formyl proton) with relative intensities of 5:1:1, respectively.

(8) Products obtained from the oxidation of N-ethylaniline

Solutions of substrate ($1x10^{-2}$M) and oxidant ($1x10^{-3}$M), taken in aqueous methanol (60%, v/v), containing NaOH(0.01 M) and KCl (ionic strength adjusted to 0.1 M),

were mixed and kept at 35°C for 24h, under nitrogen. The solvent was removed, the residue was washed with dilute HCl, and then concentrated. The crude product was distilled under reduced pressure. The distillate was crystallized from a 1:1 mixture of toluene and petroleum ether at 0°C to give the product, formanilide (yield ~70%, mp 50°C), identified by IR analysis (6c) and by NMR analysis in CCl_4 which gave peaks at 6.8 δ (aromatic protons), 3.8 δ (N-H proton) and 9.5 δ (formyl proton) with relative intensity signals of 5:1:1, respectively.

The second product (yield ~10%) was characterized as formaldehyde, which existed in water largely as the hydrate, $CH_2(OH)_2$. IR analysis did not show any carbonyl band. On evaporation of the aqueous solution of formaldehyde, a solid residue was left behind, which, on recrystallization from ether, gave crystalline needles of 1,3,5-trioxane (mp 64°C).

(9) Product obtained from the oxidation of N,N-dimethylaniline

Solutions of the substrate (1×10^{-2} M) and oxidant (1×10^{-3} M), taken in aqueous methanol (60%, v/v), containing NaOH (0.01 M) and KCl (ionic strength adjusted to 0.1 M), were mixed and kept at 35°C for 24h, under nitrogen. The solvent was removed, the residue was washed with dilute HCl, and then concentrated. The residue was distilled (yield ~75%), and identified as the N-acyl derivative, N-methylformanilide

(bp 243°C). The structure was confirmed by (a) IR analysis (IR-297, Perkin Elmer) which gave bands at 2940, 1670, 1590, 1490, 1450, 1350, 1270, 1110, 1090, 1030, 980 and 760 cm^{-1}; (b) UV analysis (UV-26, Beckman) in methanol, gave an absorption band at 235 nm; (c) NMR analysis (EM-390, 90 MHz) taken in CCl_4, gave peaks at 6.8 δ (aromatic protons), 2.8 δ (methyl protons) and 9.5 δ (formyl proton), with relative signal intensities of 5:3:1, respectively.

(10) Products obtained from the oxidation of N,N-diethylaniline

Solutions of the substrate ($1x10^{-2}$M) and oxidant (1×10^{-3}M), taken in aqueous methanol (60%, v/v), containing NaOH(0.01 M) and KCl(ionic strength adjusted to 0.1 M), were mixed and kept at 35°C for 24h, under nitrogen. The solvent was removed. The reaction mixture, possessing an acetaldehyde odour, was divided into four parts:

(i) 2ml of the reaction mixture was mixed with 5 ml of cold water. This solution, on testing for acetaldehyde by the p-phenylphenol-sulfuric acid method (7), exhibited a strong positive reaction not obtained with a N-diethylaniline blank.

(ii) 2 ml of the reaction mixture was mixed with 5 ml of 0.4% dimedone solution buffered to pH 5.0 with 0.2 M acetate. A precipitate of the dimedone derivative of

acetaldehyde was formed, which was recrystallized from ethanol (mp 141°C, lit. value, 140°C). This derivative was converted to the anhydride by boiling it (0.1g) for 3h in a mixture of 7 ml ethanol and 10 ml of 1N HCl, and later diluting with 20 ml water (mp 175°C, lit. value, 175-176°C).

(iii) Characterised as formaldehyde, in its hydrated form, $CH_2(OH)_2$. IR analysis did not show any carbonyl band. On evaporation of the aqueous solution of formaldehyde, a solid residue was left behind, which, on recrystallization from ether, gave crystalline needles of 1,3,5-trioxane (mp 64°C).

(iv) distillation of product afforded material which on crystallization from a 1:1 mixture of toluene and petroleum ether at 0°C gave formanilide (mp 50°C), identified by IR analysis (6c), and by NMR analysis in CCl_4 which gave peaks at 6.8δ (aromatic protons), 3.8δ (N-H proton) and 9.5δ (formyl proton) with relative intensities of 5:1:1, respectively.

The yields were as follows: formanilide(~70%), acetaldehyde (~10%), formaldehyde (~10%).

(11) Product obtained from the oxidation of diphenylamine

Solutions of substrate ($1x10^{-2}$M) and oxidant ($1x10^{-3}$M), taken in aqueous methanol (70%, v/v), containing NaOH (0.1 M) and KCl (ionic strength adjusted to 0.1 M), were mixed at 50°C and maintained under a nitrogen atmosphere for 24 h. The reaction mixture was cooled, filtered and

concentrated. The residue was extracted with chloroform, dried over anhydrous Na_2SO_4, and then concentrated. TLC analysis of the residue, using benzene as the developer, gave a single spot. The product, obtained in about 80% yield, was characterized by mp (147°C, decomposes), IR analysis (6d), and by uv analysis (6d) in dioxan which gave a peak at 295 nm. The product sample was confirmed to be tetraphenylhydrazine.

(12) Products obtained from the oxidation of benzylamine

Solutions of substrate (1.0 M) and oxidant ($1x10^{-2}$ M), taken in aqueous methanol (60%, v/v), containing NaOH (pH 12.0), and KCl (ionic strength adjusted to 0.1 M), were mixed and kept at 60°C for 24 h, under nitrogen.

(i) the evolution of ammonia was shown by partial distillation of the reaction mixture. The ammonia formed was absorbed in an excess of standard acid (0.1N HCl). The excess of acid was then back-titrated (against base) in the presence of methyl red indicator (4b).

(ii) The reaction mixture was treated with chloroform, the organic layer was washed with water, dried over anhydrous $MgSO_4$, and then concentrated. Spotting on TLC plates gave a single spot. IR analysis exhibited a carbonyl band at 1700 cm^{-1} and other bands that were characteristic of benzaldehyde.

(iii) The reaction mixture was treated with an acidic solution of sodium bisulfite, and cooled in ice. 25 ml of 2,4-dinitrophenylhydrazine solution (0.05 M) was added, and the mixture allowed to stand overnight at $0^{\circ}C$. The solid compound formed was filtered, dried and weighed as the 2,4-dinitrophenyl hydrazone derivative of benzaldehyde (mp $237^{\circ}C$; yield $\sim 80\%$).

(13) Product obtained from the oxidation of thiomalic acid

Solutions of substrate ($1x10^{-2}M$) and oxidant ($1 \times 10^{-3}M$), taken in 0.1M HCl (ionic strength adjusted to 0.05 M by the addition of KCl), were allowed to react at $35^{\circ}C$ for 24h, under nitrogen. At the end of the reaction, the solution was extracted with ether, washed with water, the ether evaporated, and the residue refluxed with toluene for 1h. On concentration of the toluene solution and cooling overnight, crystals of the disulfide product, dithiodimalic acid, were precipitated, which were re-crystallized from ether (mp $167^{\circ}C$; yield $\sim 75\%$).

(14) Product obtained from the oxidation of thioglycolic acid

Solutions of substrate (0.1 M) and oxidant ($1.5x10^{-3}M$), taken in 0.1M HCl (ionic strength adjusted to 0.05 M by the addition of KCl) were mixed, and allowed to react at $35^{\circ}C$ for 24 h under nitrogen. The precipitate formed was filtered dried, and recrystallized from ethanol to give the product,

dithiodiglycolic acid (mp 108°C, yield ~75%).

(15) Product obtained from the oxidation of thiophenol

To 2.2g (0.02 mole) of thiophenol, taken in 80% methanol (v/v), was added 3.3g (0.01 mole) of hexacyanoferrate(III), taken in 80% methanol (v/v) and 0.1M HCl (ionic strength adjusted to 0.005M by the addition of KCl). The reaction mixture was allowed to stand at 35°C for 24h, under nitrogen. To the reaction mixture was added 30 ml of 50% aqueous ethanol. The solution was warmed to 35°C, and the ethanol layer was separated. When the oily portion, insoluble in aqueous ethanol, was allowed to stand at room temperature (20°C) for 3h, 1.5g of diphenyl disulfide separated out. The product was recrystallized from aqueous ethanol (mp 61°C) and characterized by IR and UV analyses. IR analysis (IR-297, Perkin Elmer) gave peaks at 3060, 1580, 1480, 1295, 1180, 895, 735 and 685 cm^{-1}. UV analysis (uv-26, Beckman) in 90% ethanol (v/v) gave an absorption peak at 240 nm.

(16) Product obtained from the oxidation of sulfite

Solutions of substrate ($1x10^{-2}$ M) and oxidant ($1x10^{-3}$M), taken in 0.1M NaOH (ionic strength adjusted to 0.05 M by the addition of KCl), were mixed, and allowed to react at 35°C for 24h, under nitrogen. At the end of the reaction, the solution containing the product was treated with dilute sulfuric acid. The dithionic acid was liberated.

The solution was concentrated by evaporation, when SO_2 was evolved. This confirmed the formation of dithionate ions, from the oxidation of sulfite by hexacyanoferrate (III).

(17) Product obtained from the oxidation of thiosulfate

Solutions of substrate (0.5M) and Oxidant ($1x10^{-3}$M), taken in 0.1M NaOH (ionic strength adjusted to 0.05 M by the addition of KCl), were mixed, and allowed to react at 35°C for 24h, under nitrogen. At the end of the reaction, the solution containing the product was neutralized with dilute sulfuric acid, and then treated with a solution of Hg(I) nitrate. A yellow precipitate was formed, which turned black on heating, confirming the presence of tetrathionate ions.

(18) Products obtained from the Oxidation of Thiocyanate

Solutions of substrate (2.0 M) and oxidant (1×10^{-3}M), taken in NaOH(0.5M), and KCl (ionic strength adjusted to 0.05 M), were mixed and kept at 50°C for 24h, under nitrogen. The reaction mixture was divided into two parts:

(i) To 5 ml of the reaction mixture was added 25 ml of 0.1 M $AgNO_3$ solution, and the mixture stirred. A white precipitate of silver cyanide was formed, which was filtered and dried. The white solid, AgCN, was characterized by IR analysis which

showed the C≡N stretching band at 2155 cm^{-1}. This was compared with the C≡N stretching of an authentic sample of AgCN which gave the band at 2151 cm^{-1} (8).

(ii) to 5 ml of the reaction mixture was added 5 ml of 0.1 N HCl and 20 ml of 0.2 M $BaCl_2$ solution. A white precipitate of $BaSO_4$ was formed, which was filtered, washed with water and dried. The weight of the precipitate of Ba SO_4 was approximately that expected from the initial concentration of the oxidant.

(19) Product obtained from the Oxidation of metabisulfite

Solutions of substrate (1 x 10^{-2}M) and oxidant ($1x10^{-3}$M), taken in 0.1M NaOH (ionic strength adjusted to 0.05M by the addition of KCl), were mixed and kept at 35°C for 24h, under nitrogen. The reaction mixture was treated with dilute sulfuric acid. The solution was concentrated by evaporation, when SO_2 was evolved. This confirmed the formation of dithionate ions, from the oxidation of metabisulfite by hexacyanoferrate (III).

Tests for Radical formation:

Most of the oxidation reactions investigated were observed to proceed via radical intermediates formed in the rate determining step of these reactions. The presence of these radical intermediates was confirmed by the following :

(a) Reduction of inorganic ions, $R^{\bullet} + M^{(n+1)+} \longrightarrow R^{+} + M^{n+}$. Mercuric chloride was easily reduced by these radicals to insoluble mercurous chloride, which was relatively inert towards reoxidation by the oxidant M^{n+} .

(b) Polymerisation of an added olefinic monomer, such as acrylonitrile or acrylamide.

Acrylamide and the substrate were placed in the lower part of a Thunberg tube (9), with the oxidant solution placed in the upper portion of the tube. The system was evacuated, filled with dry nitrogen, and then sealed. The two solutions were mixed and allowed to stand at the reaction temperature. After 30 minutes, there was the formation of a white opalescence, indicating the formation of a polymer.

ESR measurements

The presence of radical intermediates formed in the rate determining steps of these reactions was detected and confirmed by esr measurements.

Using the requisite reaction conditions, the radicals were generated (flow system) by mixing the substrate and oxidant, by volume, in an esr sample tube just outside the cavity of the spectrometer. The mixture was placed under high vacuum, in order to expel dissolved oxygen, and the sample

tube was placed in the cavity of the spectrometer. The conditions for obtaining the spectrum at room temperature were as follows:

Scan range 4000 G, field set 3300 G, modulation amplitude 6.3 G, microwave frequency 9.45 GHz , time constant 0.3 Sec, scan time 4 min.

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CHAPTER 1

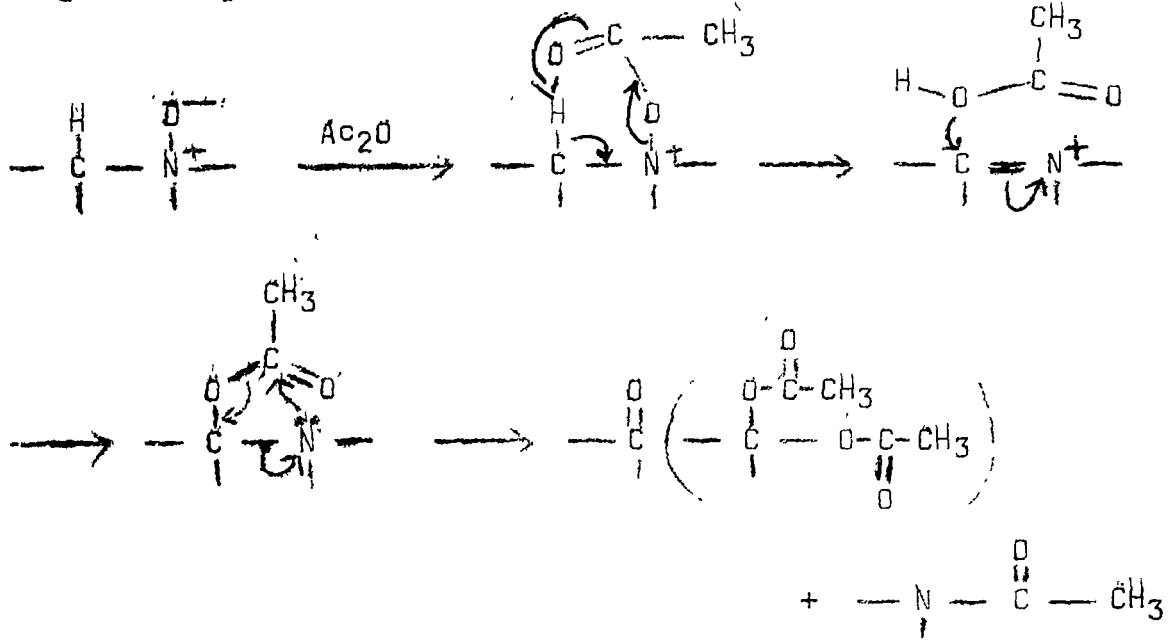
KINETICS OF OXIDATION OF SOME ALIPHATIC AMINES

The mechanism by which a one-electron oxidizing agent reacts with amines in general, has been a subject of continuing interest. The reactions of aliphatic amines with a variety of oxidizing agents, have been of considerable significance, both with regard to the kinetic aspects and to the synthetic utility of such oxidation reactions.

EARLIER WORK

The oxidation of amines can be considered to occur either by a one-electron process, or by a two-electron process. In particular, amine oxide or hydroxylamine formation has been taken as evidence of two-electron transfer pathways in amine oxidations by hydrogen peroxide (1,2), peroxyacids (1,3,4), and ozone (1,5). Amine oxides and alkyl cleavage products were predominant for the ozonization of aliphatic amines (6-11). An amine oxide appears to be a crucial link in the biogenetic interrelationships of many alkaloids (12-17). The point of oxidation of the vast majority of alkaloids is

the carbon atom that is either bonded to a nitrogen or can be placed in close proximity to it. Each of the oxidized groups can be derived from a carbinolamine, which in turn can be obtained from the rearrangement of an amine oxide. The rearrangement of an amine oxide to a carbinolamine is not an uncommon phenomenon, the Polonovski rearrangement(18) being an example of such a transformation.



The products obtained are the ketone or aldehyde, and a secondary amine.

The mercuric acetate oxidation of a variety of cyclic tertiary amines to enamines was shown to occur with the concurrent two-electron reduction of mercuric ion to metallic mercury (19-29). Electron pair transfer was advanced as the likely explanation for the oxidations of tertiary amines by cyanogen bromide (30), aqueous bromine (31), and

nitrous acid (32). Tertiary amines were oxidized to N-oxides by t-butyl hydroperoxides at low temperatures in the presence of vanadium or molybdenum catalyst (33,34).

The one-electron oxidation reactions of amines were attributed to hydrogen atom transfer which directly gave a neutral radical intermediate capable of undergoing further oxidation (35-38) or of coupling (39,40).

Aliphatic amines were oxidized by manganese dioxide in moderate yields to the corresponding carbonyl compounds (41), and spectral evidence for an imine precursor was reported (42). A series of tri-N-alkyl-amines, R_3N, where R = n-C_3H_7 through n-C_7H_{15} gave the respective formamides, R_2N-CHO, in yields improving with an increase in the chain length (36). Variation of conditions for $(n\text{-}C_4H_9)_3$ N showed better yields at higher temperatures (36). The oxidation was observed to be via the carbinolamine and enamine intermediates (31). The oxidation of aliphatic amines by Mn(III) was earlier reported (43).

Aliphatic amines have been oxidized by permanganate to a mixture of products. The reactions were sometimes incomplete and gave a multiplicity of products. For example, diethylamine was oxidized to a mixture of acetic acid, ammonia, ethanol and acetohydroxamic acid (44). A duality of mechanism was reported in the oxidatin of aliphatic amines

with permanganate (45,46). Trialkyl-carbinyl amines were oxidized by permanganate in aqueous or acetone solution to tertiary nitroalkanes in good yields (47). The oxidation of t-butylamine to the nitro compound was much slower than the oxidation of trimethylamine, wherein the initial attack occurred at the C-H bond adjacent to the nitrogen atom(37). The oxidation of dimethylamine by permanganate has been reported (48).

Aliphatic amines were oxidized by ruthenium tetroxide, but the products were not isolated (49). The formation of intractable products probably resulted from the vigorous reaction which ensued when a good reductant (amine) was oxidized by a strong oxidant such as ruthenium tetroxide.

The oxidation of aliphatic tertiary amines in benzene by a variety of quinones were reactions of special interest because of the colours produced which were useful in characterizing these amines (50,51). The oxidation of aliphatic amines with chloranil has been reported (50,52). Under very mild conditions, the conversion of primary amines to ketones in high yields was carried out with 3,5-di-tert-butyl-1,2-benzoquinone as the oxidant (53).

Primary aliphatic amines have been oxidized to the nitroalkanes by m-chloroperbenzoic acid(3,4). The oxidation

of aliphatic amines by hydrogen peroxide, catalyzed by sodium tungstate has been reported (2,54,55).

Benzoyl peroxide has been used for the oxidation of aliphatic amines (50). The oxidation of primary aliphatic amines by nickel peroxide had yielded the nitrile (56). The oxidation of aliphatic amines by t-butyl-hydroperoxide was investigated under conditions known to promote free radical oxidations (57).

The oxidation of primary amines by N-bromosuccinimide or N-chlorosuccinimide gave the aldehydes or ketones (58,59). The process involved the removal of two electrons for each molecule of amine that was oxidized. The amine was oxidized to the imine, which on acid hydrolysis gave the carbonyl derivative (58,59).

Argentic salts have been used to oxidize amines to aldehydes and ketones (60-62). Mesitoyl glyoxal has been used for the conversion of primary amines to ketones (53).

Aliphatic amines were found to be relatively inert to oxidation by lead tetraacetate in acetic acid solution at moderate temperatures. However, refluxing in benzene solution gave nitriles from primary amines (63,64), probably by a two-step dehydrogenation process involving an unstable aldimine as the intermediate,

$$RCH_2NH_2 \xrightarrow{Pb(OAC)_4} (RCH=NH) \xrightarrow{Pb(OAC)_4} RCN \ .$$

The oxidation of aliphatic amines by ceric ammonium nitrate in nitric acid medium has been reported (65, 66).

The oxidation of aliphatic amines by cobalt(III) in perchloric acid solution was reported to be essentially inert(67). Vanadium(V) in aqueous perchloric acid has been used for the oxidation of aliphatic amines (68,69).

The oxidative dealkylation of alkyl-cobalamines by iron(III), assisted by chloride ions, was reported (70), wherein the rate-limiting step was a one-electron transfer from the alkylcobalamine, generating a transient intermediate which underwent further reaction to give the product. Chloride ions in solution were found to greatly enhance the dealkylation rates in the reactions of alkylcobalamines by the Pt(II)/Pt(IV) couples (71,72), $AuCl_4^-$ (73) and $IrCl_6^{2-}$ (74).

The reaction of aliphatic amines with methylene iodide has been reported earlier(75). Palladium chloride and auric chloride in water were found to be effective for the oxidation of primary amines to carbonyl compounds(76).

Metal-catalyzed O_2 oxidations of aliphatic amines have been reported. The methyl group in N-methyl tertiary amines was selectively oxidized to N-formyl at ambient temperatures in benzene over platinum black (77).

Aliphatic amines have been oxidized by peroxydisulfate (78), 5-chloro-2-pentanone (79), palladium (II) Complexes (80), thallium (III) in acetic acid medium (81), pentacyanonitrosyl

ferrate (II) complex (82), carbon dioxide (83,84), crown ethers (85), hexacyanoferrate (III) catalyzed by both osmium (VIII) ion (86) and by ruthenium (III) ion (87), and by Meisenheimer complexes (88-92).

PRESENT WORK

The present work is a detailed kinetic investigation of the oxidation of some aliphatic amines by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere. The aliphatic amines chosen for purposes of oxidation were methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine.

Stoichiometry (Vide 'Experimental').

The stoichiometry of each of the reactions was determined to be

(a) Methylamine

$$CH_5N + 4Fe(CN)_6^{3-} + H_2O \rightarrow CH_3NO + 4Fe(CN)_6^{4-} + 4H^+$$

(b) Dimethylamine

$$C_2H_7N + 4Fe(CN)_6^{3-} + H_2O \rightarrow C_2H_5NO + 4Fe(CN)_6^{4-} + 4H^+$$

(c) Trimethylamine

$$C_3H_9N + 4Fe(CN)_6^{3-} + H_2O \rightarrow C_3H_7NO + 4Fe(CN)_6^{4-} + 4H^+$$

(d) Ethylamine

$$C_2H_7N + 2Fe(CN)_6^{3-} + H_2O \rightarrow C_2H_4O + NH_3 + 2Fe(CN)_6^{4-} + 2H^+$$

(e) Diethylamine

$$C_4H_{11}N + 2Fe(CN)_6^{3-} + H_2O \longrightarrow C_2H_7N + C_2H_4O + 2Fe(CN)_6^{4-} + 2H^+$$

(f) Triethylamine

$$C_6H_{15}N + 2Fe(CN)_6^{3-} + H_2O \longrightarrow C_4H_{11}N + C_2H_4O + 2Fe(CN)_6^{4-} + 2H^+.$$

Effect of substrate and oxidant

The rates of the reactions were found to be dependent on the first powers of the concentrations of both, substrate and oxidant (Tables 1-3).

Table 1 : Effect of substrate and oxidant

/Substrate/ (10^3x M)	/ $K_3Fe(CN)_6$ / (10^4xM)	10^5 x k_{obs} (s^{-1}) Methylamine	Dimethyl-amine
5.0	5.0	3.8	2.3
10.0	5.0	7.8	4.7
25.0	5.0	19.0	12.0
50.0	5.0	38.5	23.8
100.0	5.0	78.0	48.0
10.0	1.0	7.8	4.6
10.0	7.5	7.9	4.5
10.0	10.0	7.5	4.8

/ NaOH / = 0.1 M; μ = 0.5 M; temp. = 35°C.

Table 2: Effect of substrate and oxidant at 35.0°C.

/Trimethylamine/ (10^2 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^5 x k_{obs} (s^{-1})
5.0	5.0	2.8
10.0	5.0	6.0
25.0	5.0	14.3
50.0	5.0	29.0
100.0	5.0	58.0
5.0	2.5	2.8
5.0	1.0	3.0
5.0	0.5	2.7

Table 3: Effect of substrate and oxidant at 35°C.

/ Substrate/ (10^2 x M)	/ $K_3Fe(CN)_6$/ (10^3 x M)	10^6 x k_{obs} (s^{-1}) Ethyl-amine	Diethyl-amine	Triethyl-amine
5.0	5.0	2.0	7.0	34.0
10.0	5.0	4.0	14.5	68.0
25.0	5.0	10.2	35.0	170.0
50.0	5.0	20.5	72.0	350.0
100.0	5.0	40.0	145.0	700.0
5.0	2.5	2.1	7.2	34.0
5.0	2.0	2.4	7.0	34.4
5.0	1.0	2.0	7.5	34.5
5.0	0.5	2.2	7.0	34.0

Plots of k_{obs}, the pseudo-first order rate constant, against a 20-fold range of concentration of substrates, gave straight lines passing through the origin, indicating that the rate of oxidation was dependent on the first power of the concentrations of the substrates. This was further seen by the constant values of k_2, the second order rate constant.

When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant (10-fold range), indicating a first order dependence of the reaction on the concentration of the oxidant (Tables 1-3).

Effect of alkali

The rate of the reaction was independent of the concentration of alkali in the range studied, for methylamine and dimethylamine (Table 4). The oxidation of methylamine and dimethylamine was also possible with aqueous hexacyanoferrate (III), but the reactions were very slow, as seen from the relative values of the rate constants (Table 4). This showed that an alkaline pH was necessary for the facile oxidation of these amines. Though there was no dependence on / alkali / over the pH range studied, the reaction was not independent of pH, in the wider sense.

Table 4 : Effect of NaOH

/NaOH/ (M)	$10^5 \times k_{obs}$ (s^{-1}) Methylamine	Dimethylamine
0.025	7.8	4.6
0.075	7.6	4.9
0.10	7.8	4.7
0.25	7.6	4.5
0.50	7.8	4.9
1.00	7.5	4.5
0.00 (neutral medium)	0.11	0.06

/ Substrates / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 5 x 10^{-4} M; μ = 0.5 M ; temp. = 35°C.

All the other amines used (trimethylamine, ethylamine, diethylamine and triethylamine) were oxidized by aqueous hexacyanoferrate(III) in neutral medium, that is, without using any alkali (Tables 2-3).

Rate law

Under the present experimental conditions, the rate law could be expressed as:

$$\text{Rate} = -\frac{d/Fe(CN)_6^{3-}/}{dt} = k_{obs}/\text{Amine}/\ /Fe(CN)_6^{3-}/ \quad \ldots\ldots\ldots (1)$$

The pseudo-first order rate constant, k_{obs}, was calculated from the equation (92):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \quad \ldots\ldots \qquad (2)$$

(vide ' Experimental': Calculations).

Effect of temperature

The rate of the reaction was influenced by changes in temperature (Tables 5-7), and an increase in temperature resulted in an enhancement of the rate of the rdaction.

Table 5: Effect of temperature

Temp. ($\pm$ 0.1°C)	$10^5 \times k_{obs}$ (s^{-1})	
	methylamine	Dimethylamine
35.0	7.8	4.7
40.0	12.7	6.9
45.0	17.4	9.6
50.0	27.5	12.5

/ Substrates / = 1 x 10^{-2} M; / $K_3Fe(CN)_6$ / = 5 x 10^{-4} M; / NaOH / = 0.1 M; μ = 0.5 M

Table 6: Effect of temperature

Temp. (± 0.1°C)	10^5 x k_{obs} (s^{-1})
35.0	2.8
40.0	3.3
45.0	5.5
50.0	7.4

/ Trimethylamine / = 5 x 10^{-2} M; / $K_3Fe(CN)_6$ / = 5x10^{-3} M.

Table 7: Effect of temperature.

Temp. (± 0.1°C)	10^6 x k_{obs} (s^{-1})		
	Ethyl-amine	Diethyl-amine	Triethyl-amine
35.0	2.0	7.0	34.0
40.0	2.8	9.0	41.0
45.0	4.0	13.0	50.0
50.0	5.0	16.0	61.0
55.0	7.1	20.0	75.0

/ Substrates / = 5x10^{-2}M; / $K_3Fe(CN)_6$ / = 5 x 10^{-3} M.

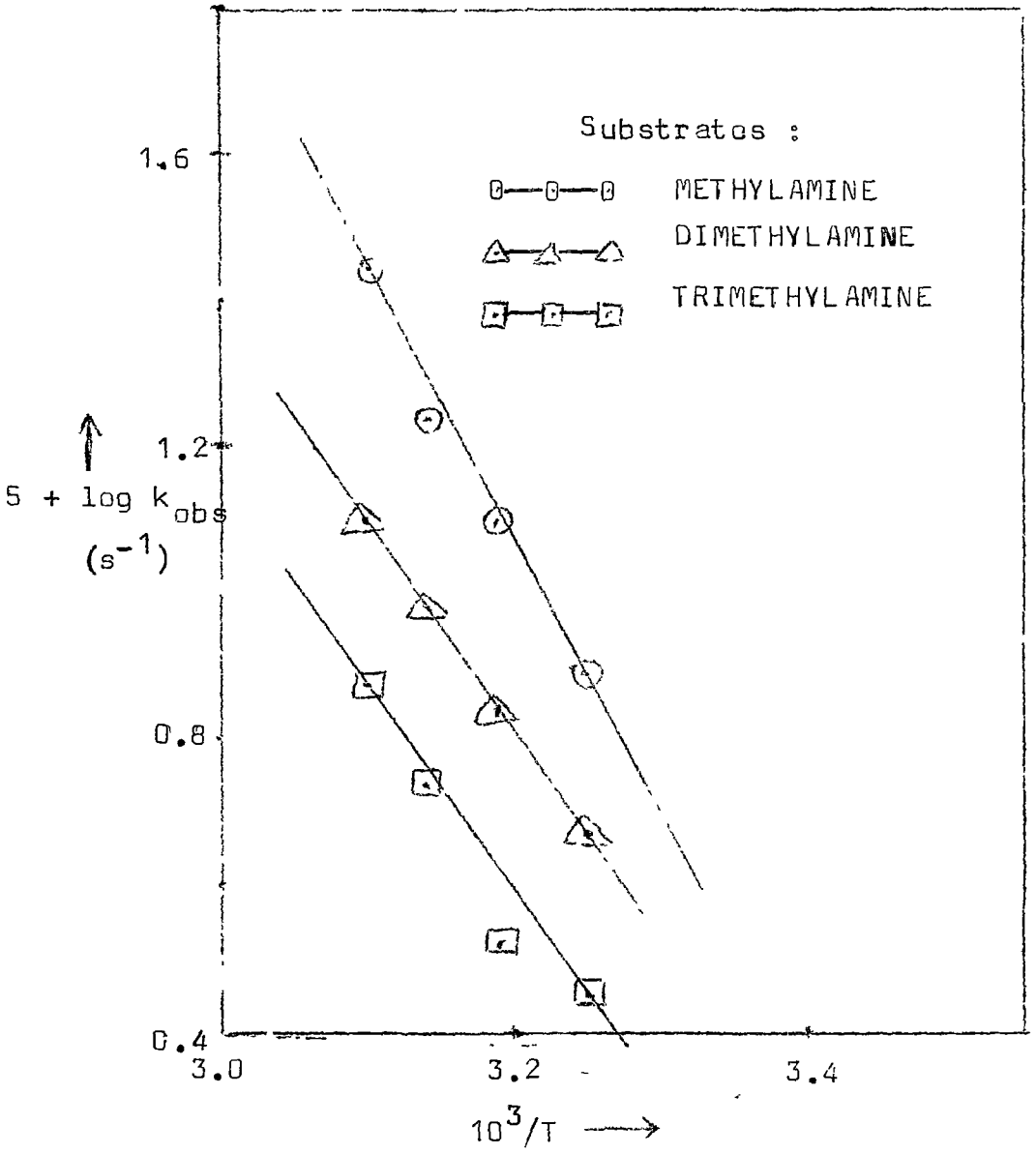


Fig. 1 . Plots of log k_{obs} against the reciprocal of temperature

Substrates : METHYLAMINE
DIMETHYLAMINE
TRIMETHYLAMINE

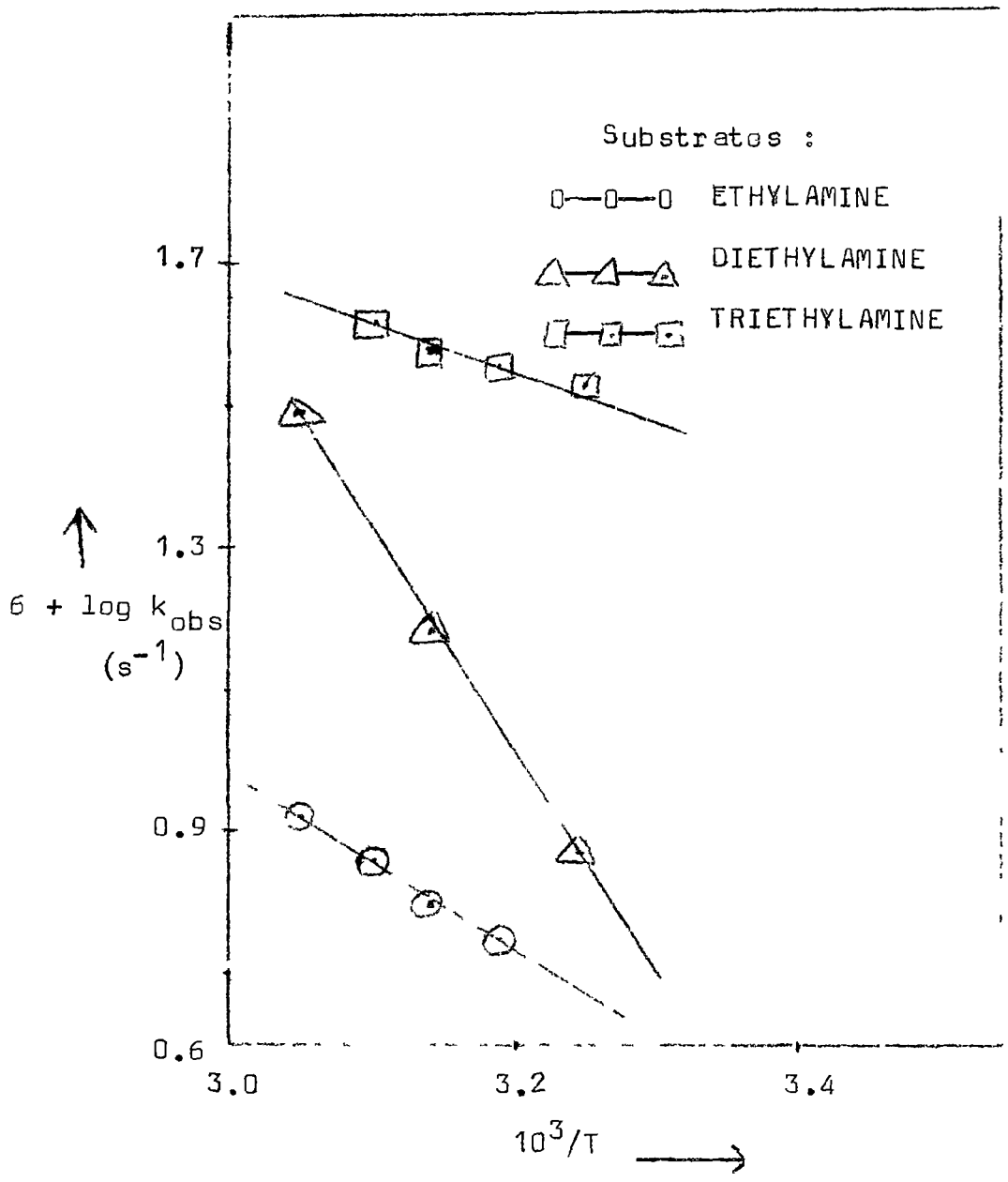


Fig. 2 . Plots of log k_{obs} against the reciprocal of temperature

Substrates : ETHYLAMINE
DIETHYLAMINE
TRIETHYLAMINE

Plots of log k_{obs} against the reciprocal of temperature were linear (Figs. 1-2), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies of the reactions. The other activation parameters were calculated (vide 'Experimental' : Calculations), and have been shown in Table 8.

Table 8: Activation Parameters

Substrate	E ($kJ\ mol^{-1}$)	A (s^{-1})	$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)
Methylamine	72±3	$1x10^{8}$	69±3	-97±4
Dimethylamine	55±2	$9x10^{4}$	52±2	-157±5
Trimethylamine	57±2	$1x10^{5}$	54±2	-154±4
Ethylamine	55±2	$4x10^{3}$	52±2	-110±5
Diethylamine	45±2	$3x10^{2}$	42±2	-130±5
Triethylamine	38±2	$1x10^{2}$	35±2	-160±5

The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were favourable for electron abstraction processes. The favourable enthalpy for electron abstraction may be in part due to the release of energy on solvation of charges created in the transition state. Values of $\Delta S^{\neq}$ in this range for radical reactions have been ascribed (93) to the forbidden nature of electron-pairing

and electron-unpairing processes, and to the loss of degrees of freedom, formerly available to the reactants, on the formation of a rigid transition state.

The activation energy for methylamine was 72 kJ mol^{-1}, while the activation energies for dimethylamine and trimethylamine were almost equal. The lower values of the activation energies for dimethylamine and trimethylamine would be due to the presence of two or more methyl groups. The electron-donating character of the methyl groups would tend to weaken the C-H bond considerably. This would enable the cleavage of the C-H bond in the slow step, resulting in the formation of a radical intermediate. In the case of methylamine, due to the presence of one methyl group, cleavage of the C-H bond would require a higher energy of activation. The larger negative values of $\Delta S^{\neq}$ for dimethyl- and trimethylamine, as compared to that for methylamine, would suggest a more facile formation of the transition state in the case of dimethylamine and trimethylamine, than for methylamine.

Effect of added $K_4Fe(CN)_6$

The addition of $K_4Fe(CN)_6$ in the concentration range, 1.0×10^{-4} M to 1.0×10^{-3} M, did not have any effect on the rates of these reactions, in the case of all the amines.

Effect of ionic strength

In the case of the oxidation of methylamine and dimethylamine by alkaline hexacyanoferrate (III), the effect of ionic strength was studied. Variations in the ionic strength of the medium using $NaClO_4$ (μ = 0.01M to 0.50 M) did not have any effect on the rates of these reactions.

Effect of added salts

The addition of salts such as NaCl, KCl, $NaNO_3$, KNO_3, Na_2SO_4, $MgSO_4$ (concentration range of 1.0×10^{-4}M to 5.0×10^{-3}M), did not have any effect on the rates of the oxidation reactions of these amines.

Radical intermediates

The esr spectra of the corresponding radicals, generated from the oxidation of each of the substrates, were obtained (vide 'Experimental': ESR measurements).

(1) From the oxidation of methylamine and dimethylamine

The esr spectra of the radicals obtained from the oxidation of methylamine and dimethylamine, gave 3 spectral lines with peak heights of 1:2:1. This was the peak height distribution for an unpaired electron in the environment of two equivalent hydrogen atoms. The following conclusions can be drawn from these spectra:

(a) the stable radical is formed by the loss of a hydrogen atom adjacent to the amine nitrogen atom;

(b) the interaction of the unpaired electron extends to the hydrogen atom on the same carbon atom;

(c) the hydrogen attached to the nitrogen atom does not interact with the unpaired electron to give hyperfine splitting.

(2) From the oxidation of trimethylamine

The esr spectrum of the radical generated from the oxidation of trimethylamine gave 9 spectral lines. The unpaired electron was subject to a strong interaction with the nitrogen atom (I = 1, a_N = 10 gauss),and weaker interactions with two magnetically equivalent protons (I = 1/2, a_H = 1.5 gauss). The spectrum observed consisted of 3 main lines of equal intensity, 10 gauss apart, each of which was further split into a 1:2:1 triplet, the lines of which were separated by 1.5 gauss.

(3) From the oxidation of ethylamine

The esr spectrum of the radical generated from the oxidation of ethylamine gave an 8-line spectrum, corresponding to the paramagnetic species, $C_2H_5\overset{\bullet+}{N}H_2$. The isotropic coupling constants were 18.8G for the nitrogen, 21.5G (amino protons), 33.5 G(methyl protons) and 24.5 (methylene protons).

(4) From the oxidation of diethylamine

The esr spectrum of the radical generated from the oxidation of diethylamine gave a 12-line spectrum, corresponding to the paramagnetic speccies, $(C_2H_5)_2 \overset{\bullet +}{N}H$. The isotropic coupling constants were 18.6G for the nitrogen, 22.2 G(N-H proton), 37.1G (methyl protons) and 27.5 G (methylene protons).

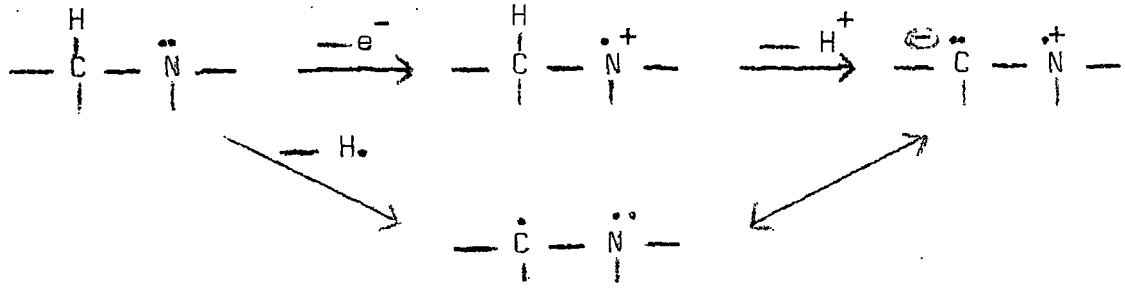
(5) From the oxidation of triethylamine

The esr spectrum of the radical generated from the oxidation of triethylamine showed that the paramagnetic species present was $(C_2H_5)_3 \overset{\bullet +}{N}$. The isotropic coupling constants were 18.0 G (nitrogen), 22.3G (methyl protons) and 26.5 (methylene protons). The spectrum was resolved into 3 groups of lines, with each group having equal intensity. This triplet was explained by the interaction of the unpaired electron in the radical with a nucleus of spin 1, presumably nitrogen. A total of 16 lines was observed within each group, of which the centre two lines were of equal intensity, indicating an interaction with an odd number of protons. A species, $(C_2H_5)_3 \overset{\bullet +}{N}$, with 15 protons, was thus inferred.

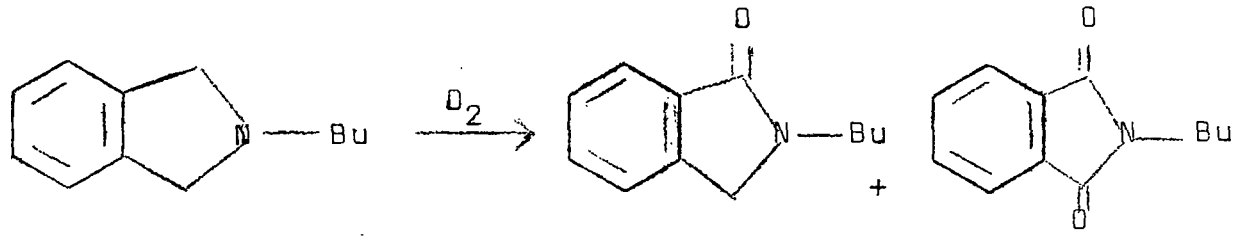
Mechanism

The susceptibility of an amine to oxidation can be attributed to the availability of the unshared pair of

electrons on the nitrogen atom. Generally, the first step in the oxidation of an amine involves the transfer of one or both of the electrons to the oxidant, followed by an elimination of a proton to give a carbon radical or a carbonium ion. In some cases, the removal of the α-hydrogen is the initial step. Assuming that the oxidation is a one-step process, the two key steps can be depicted in the following manner (38):



The conversion of N-n-butylisoindoline(I) to N-n-butylphthalimidine (II) and N-n-butylphthalimide (III) by oxygen in methyl isopropyl ketone at 38°C illustrated the above-mentioned two steps by which the oxidation of an amine could be initiated (38).



(I) (II) (III)

In principle, the oxidation of an amine to an amide parallels the oxidation of a primary alcohol to a carboxylic acid.

$$RCH_2OH + H_2O \longrightarrow RCOOH + 4H^+ + 4e^-$$

$$RCH_2NH_2 + H_2O \longrightarrow RCONH_2 + 4H^+ + 4e^- .$$

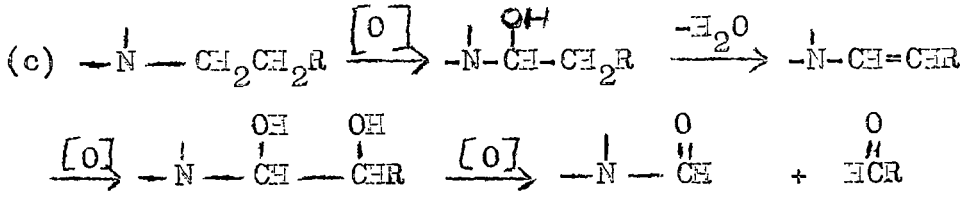
However, in practice, a variety of products may be obtained, depending on the structure of the amine. When the amine is a primary amine and has a pair of α-hydrogen atoms, it is generally oxidized to a carboxylic acid with the elimination of ammonia. The reaction can be envisaged as proceeding through a carbinolamine that undergoes C-N bond cleavage, much more rapidly than oxidation, to give an amide. The aldehyde that is formed from the scission of the C-N bond is oxidized further to the acid.

$$RCH_2NH_2 \xrightarrow{[O]} \underset{OH}{RCH}-NH_2 \longrightarrow RCHO \xrightarrow{[O]} RCOOH$$
$$+$$
$$NH_3$$

There are three main types of conversion in the oxidation of an amine. They are:

(a) $$-\overset{|}{N}-CH_3 \xrightarrow{[O]} -\overset{|}{N}-\underset{OH}{CH_2} \xrightarrow{[O]} -\overset{|}{N}-\overset{O}{\overset{\|}{C}}H$$

(b) $$-\overset{|}{N}-CH_2R \xrightarrow{[O]} -\overset{|}{N}-\underset{OH}{CHR} \longrightarrow -\overset{|}{N}- + \overset{O}{\overset{\|}{C}}H + \overset{O}{\overset{\|}{C}}H-R$$



In all three types of conversions, it is assumed that the first step involves the oxidation of the amine to a carbinolamine. In type (a), the carbinolamine is oxidized further to give an N-acyl derivative. In type (b), the carbinolamine rearranges to give a secondary amine and an aldehyde. In type(c), water is eliminated from the carbinolamine, and the resultant enamine is oxidized further to afford an N-acyl derivative and a carbonyl compound. The Oxidation of the enamine most likely involves hydroxylation of the double bond followed by oxidative cleavage of the resultant α-glycol. The three types of conversions (a,b and c), involve the removal of four electrons, two electrons and six electrons, respectively, from the starting compound.

With regard to mechanisms, one-electron oxidants may attack the amine at the nitrogen or at an α-hydrogen atom. The mode of attack will depend on the structure of the amine as also on the nature of the oxidant.

(1) Oxidation of methylamine, dimethylamine and trimethylamine

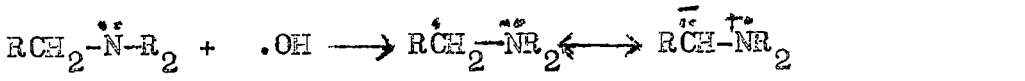
The rates of the oxidation reactions of all these amines by hexacyanoferrate (III) were dependent on the first powers of the concentrations of the substrate and oxidant (Tables 1-2). This indicated that the reaction was directly between the substrate and oxidant.

The addition of hexacyanoferrate (II) ions did not have any effect on the rates of the reactions. This showed that the first step between the substrate and hexacyanoferrate (III) (which was the electron-abstraction step), was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, indicating that the reaction was between an ion and a neutral (dipolar) species.

The mechanism of the reaction could be envisaged as proceeding via the removal of the α-hydrogen in the initial step, giving a radical intermediate, the aminoalkyl radical. It has been observed that the irradiation of dimethylamine and trimethylamine in neutral or alkaline media with high-energy electrons (94) gave the aminoalkyl radicals ($R_2-N-\dot{C}H_2$), since the abstraction of the α-hydrogen was favoured due to the resonance stabilizing effect of the

adjacent nitrogen lone pair



..... (1)

The γ-irradiation of primary amines frozen at 77K gave alkylamino radicals ($R_2\dot{C}H-\ddot{N}H$), which isomerized to aminoalkyl radicals ($R_2-\dot{C}-NH_2$) on warming (95). Under these conditions, dimethylamine gave the radical, $\dot{C}H_2NHCH_3$, and trimethylamine gave the aminoalkyl radical, $\dot{C}H_2N(CH_3)_2$ exclusively (95). The results of γ-irradiation of amines adsorbed on silica gel at 77K were similar(96).

In the present investigation, the radical intermediates obtained from the oxidation of methylamine, dimethylamine and trimethylamine, respectively, were characterized by ESR spectroscopy (vide 'Radical Intermediates').

The subsequent steps were rapid, and no intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the carbinolamines (A, B and C, respectively), were not successful. It could be postulated that the carbinolamines, when formed as intermediates, would be rapidly oxidized to the N-acyl derivatives, respectively.

The reaction sequences for the oxidation of these amines by hexacyanoferrate(III) have been shown in Schemes 1-3.

SCHEME 1

Oxidation of Methylamine

$$CH_3NH_2 + Fe(CN)_6^{3-} \xrightarrow{\text{SLOW}} \dot{C}H_2NH_2 \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}}$$

$$\overset{+}{C}H_2NH_2 \xrightarrow{H_2O} \underset{\displaystyle OH}{\overset{\displaystyle CH_2NH_2}{|}} \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}}$$

(A)

$$\underset{\displaystyle OH}{\overset{\displaystyle \dot{C}H-NH_2}{|}} \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} \underset{\displaystyle OH}{\overset{\displaystyle \overset{+}{C}H-NH_2}{|}} \xrightarrow[(-H^+)]{} \underset{\displaystyle O}{\overset{\displaystyle HC-NH_2}{\|}}$$

(I)

SCHEME 2

Oxidation of Dimethylamine

$$(CH_3)_2NH + Fe(CN)_6^{3-} \xrightarrow{\text{SLOW}} CH_3-\underset{\displaystyle \dot{C}H_2}{\overset{\displaystyle H}{\overset{|}{N}}}-H$$

$$\xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} CH_3-\underset{\displaystyle \overset{+}{C}H_2}{\overset{\displaystyle H}{\overset{|}{N}}}-H \xrightarrow{H_2O} CH_3-\underset{\displaystyle CH_2OH}{\overset{\displaystyle H}{\overset{|}{N}}}-H$$

(B)

$$\xrightarrow[\text{fact}]{Fe(CN)_6^{3-}} CH_3-\underset{\displaystyle \dot{C}HOH}{\overset{\displaystyle H}{\overset{|}{N}}}-H \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} CH_3-\underset{\displaystyle \overset{+}{C}HOH}{\overset{\displaystyle H}{\overset{|}{N}}}-H$$

$$\xrightarrow[(-H^+)]{} CH_3-\underset{\displaystyle CHO}{\overset{\displaystyle H}{\overset{|}{N}}}-H$$

SCHEME 3

Oxidation of Trimethylamine

$$(CH_3)_3\,N + Fe(CN)_6^{3-} \xrightarrow{SLOW} (CH_3)_2\,N\text{-}\dot{C}H_2$$

$$\xrightarrow[fast]{Fe(CN)_6^{3-}} (CH_3)_2\text{—}\overset{+}{N}CH_2 \xrightarrow{H_2O} (CH_3)_2\text{—}N\text{-}CH_2OH$$

(C)

$$\xrightarrow[fast]{Fe(CN)_6^{3-}} (CH_3)_2\text{—}N\dot{C}HOH \xrightarrow[fast]{Fe(CN)_6^{3-}} (CH_3)_2\text{—}N\text{-}\overset{+}{C}HOH$$

$$\xrightarrow[(-H^+)]{} (CH_3)_2\text{—}N\text{-}CHO$$

(III)

The reaction sequences (Schemes 1-3) show mechanistic pathways involving the removal of four electrons from the starting compound, which would be in agreement with the stoichiometries of these reactions. The oxidation of methylamine to formamide (I), of dimethylamine to formylmethylamine (II), and the oxidation of trimethylamine to formyldimethylamine (III), constitute examples of reactions wherein the oxidation occurs at the N-alkyl side chains, leading to N-aldehydes.

The product obtained from the oxidation of each of the amines, was isolated and characterized by spectral methods (vide 'Experimental' : Product Analysis).

(2) Oxidation of ethylamine, diethylamine and triethylamine

The rates of the oxidation reactions of all these amines by hexacyanoferrate (III) were dependent on the first powers of the concentrations of the substrate and oxidant (Table 3). This indicated that the reaction was directly between the substrate and oxidant.

The addition of hexacyanoferrate (II) ions did not have any influence on the rates of the reactions. This showed the irreversibility of the initial electron-abstraction step between the substrate and oxidant.

The addition of salts did not have any effect on the rate of the reaction, indicating that the reaction was between an ion and a neutral (dipolar) molecule.

The mechanism of the reaction was envisaged as proceeding via the transfer of one electron, from the nitrogen atom of the amine, to the oxidant. This would result in the formation of the cation radical intermediate (aminium cation radical). Aminium radicals were first proposed for the Hofmann-Loffler preparation of N-methyl-granatamine (97). Related aryldialkyl aminium radicals were postulated to

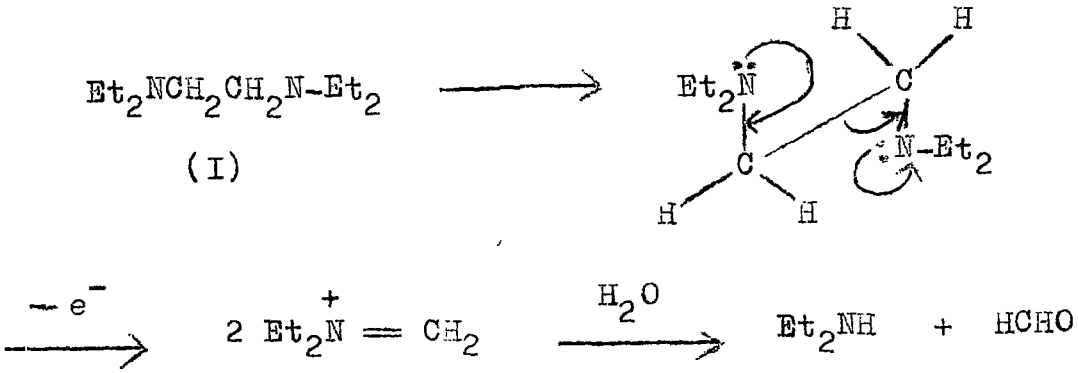
explain the effects of a series of oxidants on tertiary amines (98). Aminium radicals were shown to be generated from the oxidation of alkylamines and arylalkylamines, wherein the one-electron reagent directly removed an electron from an amine,

$$R_3N: + X\cdot \longrightarrow R_3N^{+\cdot} + X:^-$$

The oxidizing agents which have been used to generate aminium radicals from alkyl amines or arylalkyl amines have included nitrogen dioxide in CCl_4 (99, 100), N-bromosuccinimide in CCl_4 (101), metal-catalyzed oxidations by oxygen in benzene-methanol (102), silver ions in acetonitrile(103), N-chloro-benzotriazole in benzene(104), permanganate(46), chlorine dioxide (105-112), iron (III) complexed with various substituted phenanthrolines (113), octacyanomolybdate(V) complex (113), and hexacyanoferrate (III) in alkaline medium (113-116). Aminium radicals are of interest not only because they are isoelectronic with alkyl radicals, but also because these species have been used as chain-carrying intermediates in novel synthetic applications (117-126).

Geometrical factors influencing the stability of non-aromatic aminium radicals have been extensively investigated using cyclic voltammetry (127) and photoelectron spectroscopy (128). The stability of the radicals, formed from complex

polycyclic tertiary amines, was shown to depend on favourable alignments for the lone pair $-\sigma_{CC}$ interactions, which favoured through-bond interactions rather than through-space interactions(127,128). The oxidation of cyclic and noncyclic polyamines by linear sweep voltametry showed that the introduction of an electron withdrawing heteroatom into a tertiary amine, destabilized the aminium radical and raised the oxidation peak potential (129). The net effect was the stabilization of the incipient radical cation as a result of through-bond interactions (129). The low peak potential of N, N, N′, N′- tetraethyl-1,2-diaminoethane (I), relative to triethylamine, was attributed to stabilization by a through-bond interaction between the nitrogen atoms. This was substantiated by the isolation of formaldehyde as the carbonyl oxidation products (129). Thus, the oxidation proceeded via a Grob fragmentation (Scheme) , which had the same stereochemical requirement as a through-bond interaction (130).



(SCHEME)

It was reported that amines containing the β-chloroethyl group underwent both α- and β-chlorination in CCl_4; hydrolysis of the resultant products produced aldehydes and secondary amines (131). The oxidative dealkylation of tertiary amines in acidic aqueous hypochlorous acid solution gave a product which could have been formed either by abstraction of an α-proton or by an electrophilic attack on the α-carbon (131). There was a greater tendency towards N-methyl oxidation by hypochlorous acid (31) and by chlorine dioxide(112). N-haloamides were observed to oxidize tertiary amines in a manner very similar to that of hypohalous acid. Such reactions were usually performed in aqueous media, resulting in the formation of vinylamine type of products (132,133). The gas phase reactions of triethylamine (35) and trimethylamine (35) with oxygen had indicated two concurrent oxidation pathways in the early stages. The overall process produced mainly ethylamine and acetaldehyde. The reaction rates of atomic oxygen (from $N + NO \rightarrow N_2 + O$) with amines, gave an order of reactivity trimethylamine $>$ dimethylamine $>$ ethylamine $>$ methylamine $>$ ammonia (134,135). The reaction products for methylamine were methane, ammonia, water, hydrogen, oxygen and the hydroxyl radical (134,135). The overall process in the anodic oxidation of tertiary alkylamines in acetonitrile or in aqueous alkaline solutions was the

oxidative dealkylation to carbonyl compounds and secondary amines (136). Secondary amines also underwent a similar dealkylation process (137). Most of the evidence presented for the mechanistic pathways supported a mechanism analogous to that proposed for chemical one-electron oxidants and did not involve electrode surface phenomena (138). Correlations of the logarithms of the rate constants of several 1-electron oxidations of amines with the amine polarographic peak potentials have been made (109). Product distribution and a low primary isotope effect for the deprotonation step, supported a transition state with a nearly intact α-C-H bond, resembling the aminium cation radical more than the α-amino radical (109).

In the present investigation, the aminium cation radicals obtained from the oxidation of ethylamine, diethylamine and triethylamine, respectively, were characterized by ESR spectroscopy (vide 'Radical Intermediates').

The subsequent steps were rapid, and no intermediate product(s) could be isolated from the reaction mixture.

The formation of the intermediates (D, E and F respectively), seemed reasonable, in view of the arguments advanced for the relative stability of such types of systems(139).

The final step of the reaction, in each case, was required as a consequence of the reaction stoichiometry and the observed reaction products.

In the present investigation, the order of reactivity of the amines with hexacyanoferrate(III) was triethylamine > diethylamine > ethylamine (Table 3). This order of reactivity was probably dictated for the most part by the ionization potentials of the amines, which follow the reverse order (140). This order of reactivity was to be expected for electron transfer from nitrogen, since the alkyl groups were electron - donating inductive substituents. Oxidative dealkylation was observed in the reactions of aliphatic amines with chlorine dioxide (105-107), and with buffered permanganate (46), wherein the involvement of aminium cation radicals was demonstrated; the reactivity was in the order

$$R_3N > R_2NH > RNH_2.$$

Oxidative dealkylation also occurred in living organisms, and was a major pathway in the metabolism of certain drugs; it has been shown to be effected by the microsomal fraction of mammalian liver (141). Oxidation at the α-carbon was also involved in the biogenesis of alkaloids; for example, the berberine bridge - carbon atom was derived from an N-methyl group (142,143).

Overwhelming evidence has been presented in earlier investigations to establish the intermediacy of the aminium cation radical as the dominant species formed in the first step of the oxidation reactions of aliphatic amines (46, 105-107, 144-150).

The sequence of reactions for the oxidation of the respective amines by hexacyanoferrate (III), is shown in Schemes 4-6.

SCHEME 4

Oxidation of Ethylamine

$$C_2H_5NH_2 + Fe(CN)_6^{3-} \xrightarrow{\text{Slow}} C_2H_5\overset{+}{\dot{N}}H_2$$

$$\xrightarrow[(\,-H^+\,)]{} CH_3\dot{C}HNH_2 \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} CH_3-\underset{H}{\overset{\downarrow}{C}} = \overset{+}{N}\begin{matrix}H\\H\end{matrix}$$

(D)

$$\xrightarrow{H_2O} CH_3\,CHO + NH_3 + H^+$$

SCHEME 5

Oxidation of Diethylamine

$$(C_2H_5)_2\text{-}NH + Fe(CN)_6^{3-} \xrightarrow{\text{Slow}} (C_2H_5)_2\text{-}\overset{\bullet}{N}\text{-}H$$

$$\xrightarrow[(-H^+)]{} C_2H_5\text{-}N(H)\text{-}\dot{C}HCH_3 \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}}$$

$$C_2H_5\overset{+}{N}(H)=CHCH_3 \xrightarrow{H_2O} C_2H_5NH_2 + CH_3CHO + H^+$$

(E)

SCHEME 6

Oxidation of Triethylamine

$$(C_2H_5)_3N + Fe(CN)_6^{3-} \xrightarrow{\text{Slow}} (C_2H_5)_3\text{-}\overset{\bullet}{N}^+$$

$$\xrightarrow[(-H^+)]{} (C_2H_5)_2\text{-}N\text{-}\dot{C}(H)\text{-}CH_3 \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}}$$

$$(C_2H_5)_2\text{-}\overset{+}{N}=C(H)\text{-}CH_3 \xrightarrow{H_2O} (C_2H_5)_2\text{-}NH + CH_3CHO + H^+$$

(F)

The products, obtained from the oxidation of each of the amines, were isolated and characterized by spectral methods (vide 'Experimental' : Product Analysis).

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CHAPTER 2

KINETICS OF OXIDATION OF SOME AROMATIC AMINES

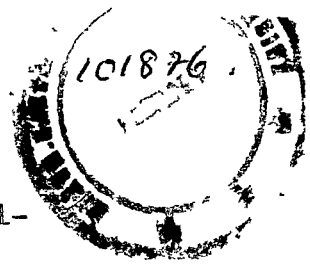
The oxidation of aromatic amines has been achieved by a variety of oxidizing agents, and the products obtained from such oxidation reactions have been observed to be dependent on the nature of the amine, the oxidizing agent, and the reaction conditions employed for these reactions.

EARLIER WORK

Primary aromatic amines gave good yields of azobenzene when oxidized by manganese dioxide (1-4). The oxidation of substituted benzylanilines with manganese dioxide gave the corresponding benzylidene - anilines in good yields (5).

The oxidation of N-benzylanilines by halogen or hypohalite showed that the hypohalite attack in methanol did not involve the formation of an N-halogenated intermediate(6).

Primary aromatic amines were oxidized by lead tetra-acetate to either azobenzenes (7,8), or to quinones and derivatives (8) as major products, depending on the ring substituents, but the yields were quite low. These oxidation reactions involved the intermediacy of the hydrazo compounds (7,8). The oxidation of phenacylanilines by lead tetraacetate



has been reported (9). The oxidation of 2,4,6-triphenyl-aniline by lead tetraacetate gave a stable radical (10).

Aromatic amines were oxidized by Cu (II) in hydroxylic solvents, in the presence of oxygen, to complex mixtures. Aniline gave quinone anil as a major product, in addition to azobenzene and phenoxazine (11).

Argentic ions have been used for the conversion of primary amines to mixtures of nitriles and aldehydes (12). The oxidation of aromatic amines by Ag(II) picolinate was suggested as a one-electron transfer process with the demonstration of the intermediacy of radical cations (13). Ring-substituted anilines were converted to the respective azobenzene on treatment with argentic oxide in benzene or ether media (14). The oxidation of ring substituted anilines by Ag_2CO_3 / celite gave azobenzenes, and the reaction was postulated to proceed by a radical coupling process(15,16).

The reaction between peroxydisulfate ion and aromatic amines in alkaline medium, known as the Boyland - Sims oxidation (17-19), was studied kinetically (20-22), wherein a general mechanism for the process was suggested. The oxidation of primary aromatic amines by peroxydisulfate in acetic acid gave N-aryl-p-benzoquinone diimines as the initial products, and the pathway was suggested to involve radical intermediates (23-26).

Anilines were oxidized to nitrobenzenes by t-butyl hydroperoxide at low temperatures in the presence of vanadium or molyndenum catalysts (27). The mechanism involved a rapid reversible formation of a peroxide - catalyst complex, followed by the rate determining nucleophilic attack of the amine lone pair and a heterolytic oxygen - oxygen bond cleavage (27). Perbenzoic acid and m-chlorobenzoic acid have been used for the oxidation of 2,4,6-tri-t-butylaniline (28) and 4-fluorenylamine (29).

Peroxyacetyl nitrate gave high yields of acetamide from primary amines (30).

Quinones and quinone imines were obtained from the oxidations of aromatic amines by potassium nitrosodisulfonate (31).

The treatment of primary amines with IF_5 gave nitriles (32,33), while carbonyl compounds were obtained from the oxidation of secondary amines (32,33) and tertiary amines(34).

The oxidation of N-alkylarylamines by chromic acid gave aldehydes in yields up to 37%; quinones and other oxidation products were also formed (35). The oxidation of N-alkyl-2,4-dinitroanilines with chromic acid was reported(36).

The oxidation of primary amines by ceric ions gave the quinone imine in 70% yield (37).

The iodination of anilines in aqueous DMSO and DMF

media (38), by N-iodosuccinimide (39) and by iodine monochloride (40) have been reported. The chlorination of anilines by chloramine-T has been studied (41).

The electrochemical oxidation of aniline at a platinum electrode has been studied (42).

The oxidation of aniline has been studied with a variety of oxidizing agents such as periodate(43), quinazolines (44), N-chlorobenzamide (45), sodium chloride (46), 1-fluoro-2,4-dinitrobenzene and 1-chloro-2,4-dinitrobenzene(47), peroxymonophosphoric acid (48), bromate ion (49), sodium iodate (50), thallium (III) ion (51), picryl chloride (52,53), phenyl-2,4,6-trinitrophenyl ethers (54), acetonaphthones in various solvents (55), substituted benzyl chlorides in methanol-acetonitrile mixtures (56), and with chloromethylated phenols (57).

The oxidation of N,N-dimethylaniline with Mn(III) acetate in acetic acid, in the presence of air, gave a product which was derived by the condensation of a formaldehyde unit with the substrate (58). The Mn(III) acetate oxidation of N,N-dialkylanilines gave N-aryl-N-alkyl acetamides in high yields (59). When oxidized by Mn(III) acetate, a series of p-substituted N,N-dialkyl-anilines gave good yields of p-substituted N-phenyl - N-alkyl acetamide (60).

N,N-dialkylanilines undergo oxidative dealkylation, on treatment with lead tetraacetate, to give N-aryl-N-alkyl acetamide as the major product (61). Based on kinetic studies of the oxidation of a number of meta- and para-substituted N,N-dimethylanilines by lead tetraacetate in chloroform/ acetic anhydride, a mechanism involving the rate determining abstraction of an electron from nitrogen to give an aminium cation radical, followed by rapid proton loss and a second (rapid) electron transfer, was proposed (62-63). The ρ value (-2.4 ± 0.5) found for ring substituted dimethylanilines indicated a high degree of positive charge on nitrogen in the transition state(63). Experimental evidence for the intermediacy of the aminium cation radicals has been obtained from electron spin resonance studies of a number of mono- , di- , and triaryl amines in solution with lead tetra-acetate (64).

The oxidation of N,N-dimethyl-aniline by $CuCl_2$ in ethanol provided evidence for multiple two-electron transfer processes in the formation of the product (65).

N,N-Dimethylalkylamines were oxidized to the respective carbonyl compounds by UF_6 , the mechanism involving a two-electron pathway via an iminium ion intermediate (66).

As an example of metal catalyzed O_2 oxidations in the liquid phase, N,N-dimethylaniline was converted to N-methyl-N-phenyl formamide, when the oxidation was carried out at ambient temperatures in benzene over platinum black (67, 68).

The oxidations of N,N-dimethylaniline and N-methyl-N-phenylaniline with peroxomonophosphoric acid (48,69) showed a rate determining nucleophilic attack of the neutral amine on the peracid oxygen, similar to that observed for other peracid oxidations of primary amines (70).

The oxidations of aromatic amines by peroxydisulfate in alkaline media (Boyland-Sims oxidation), with particular reference to ring-substituted N,N-dimethylaniline, showed that the reaction proceeded by an ipso attack with rearrangement, rather than a rate limiting attack at the ortho carbon (21).

The oxidation of a series of substituted N,N-dimethylanilines by ozone had yielded N-methyl formanilides and bis (N-methylanilino) methyl peroxides, the former product predominating in polar solvents, and the latter product becoming more important with decreasing solvent polarity (71). There was no formation of N-oxides. It was thought that both cationic and radical intermediates were involved as precursors (71).

The free energies of formation of cation radicals

and dications for a number of alkyl substituted ortho phenylene diamines by cyclic voltammetry was reported(72). The oxidation of N-substituted diaryl amines to carbazoles at a platinum anode in acetonitrile has been reported(73).

The addition of N,N-dimethylaniline to the ruthenium cation (74) and to various complexes (75), has been investigated.

The reaction of N-methylaniline with dimethyl aluminium hydride has been reported (76).

The N,N-dimethylaniline - tosyl chloride system had been used to initiate the polymerization of several vinyl polymers, and the kinetics of such polymerization reactions have been studied (77).

Kinetic isotope effects in the reactions of benzyl-benzene sulfonates with N,N-dimethylanilines have been reported (78).

Diarylamines were oxidized by nickel peroxide to tetraaryl hydrazines (79).

The electrochemical oxidation of disubstituted diphenylamines and trisubstituted triphenylamines had resulted in the formation of stable radical cations, which on further oxidation gave carbazoles (80). The anodic oxidation of para-substituted diphenylamines showed that

the initially formed cation radicals could give rise to different types of products, depending on the nature of the substituent and the alkalinity of the medium (81).

The photocyclization of N-substituted diphenylamines in non-halogenated solvents supported a mechanism involving the conversion of triplet amine to dihydrocarbazole, and subsequently to carbazole (82). In the presence of increasing amounts of CCl_4, the intramolecular triplet pathway was suppressed, and intermolecular electron transfer processes were favoured, leading to complex mixtures of products (83).

Diphenylamine was oxidized to the ketone in good yield by diphenyl selenic anhydride (84), and by diphenyl selenyl chloride (85).

The oxidation of aromatic amines adsorbed on various oxide surfaces was studied by ESR spectroscopy, and the identity of the desorbed product was shown to depend on the oxide surface. For example, diphenylamine gave diphenyl nitroxides on an alumina surface, while N,N-diphenylbenzidine was obtained when the oxidation was carried out on an alumina-silica surface (86).

The dye-sensitized photo-oxidation of diphenylamine has been reported (87).

The reaction of chlorine dioxide with a series of ring substituted N,N-dimethylbenzylamines exhibited the validity of linear free energy relationships (88). These oxidation reactions demonstrated the duality of mechanisms (electron abstraction and hydrogen abstraction), operating in chlorine dioxide oxidations (89). In both, electron abstraction and hydrogen abstraction, a planar configuration of the bonds about the nitrogen atom should be energetically favoured. These would involve Sp^2 orbitals, with the odd electron in the p-orbital.

The reactions of dimethylbenzyl amines with bromine (90), and with hypochlorous acid (88), showed a preferential benzyl cleavage, while the reaction with chlorine dioxide indicated that the cleavage was dependent on the number of α-hydrogen atoms present (88).

Benzylamine was oxidized by MnO_2 in moderate yields to the corresponding carbonyl compound, and spectral evidence for an imine precursor was reported (91).

Neutral permanganate (92,93) or alkaline permanganate (94) have been used for the oxidation of amines having hydrogen on carbon bonded to nitrogen (α-hydrogen), leading to complex mixtures of products, depending on the structure of the amine and the reaction conditions. The suggested mechanistic pathway involving the initial formation of the iminium species was also found to depend on the structure of the amine (95).

Benzylamine was oxidized to the corresponding nitrile with lead tetraacetate in refluxing benzene (96). Dibenzylamine underwent oxidative cleavage with lead tetraacetate giving benzaldehyde (60%) and benzonitrile (24%), along with smaller amounts of substituted benzylamines (96).

Cuprous chloride in pyridine, in the presence of oxygen, was used to oxidize substituted benzylamines to the corresponding benzonitriles (97).

Nickel peroxide has been used for the preparation of nitriles from substituted benzylamines (98).

Cobalt (III) in perchloric acid solution has been used for the oxidation of benzylamine, wherein the benzyl radical was stabilized by resonance, and the mechanistic pathway involved the attack at the α-C-H (99).

Benzylamine and α-methyl-benzylamine were converted to benzaldehyde and acetophenone, respectively, when the oxidations were carried out with aqueous potassium ferrate (100).

Methylbenzylamine was oxidized to the carbonyl compound when the oxidations were carried out with $PdCl_2$ in the presence of 10% palladium on charcoal (101).

Primary and secondary alkylamines and alkylarylamines (substituted benzylamines) having an α-H gave the carbonyl compound as the major product when the oxidations were carried out with, diacyl peroxides (102).

Kinetic studies and the results of substituent effects in the oxidation of benzylamines with p-nitrobenzene sulfonyl peroxide, supported a two-step, two-electron mechanism, wherein rapid nucleophilic attack by the amine gave an adduct. This was followed by the rate-determining elimination to give the imine (103).

Kinetic and isotope effect studies with substituted benzylamines and substituted arylsulfonyl peroxides supported an unsymmetrical transition state for elimination, in which the leaving group was largely removed, giving rise to substantial benzylic proton transfer (104).

Ruthenium (III) has been used as catalyst in the oxidation of benzylamines by oxidizing agents such as phenyl-iodosoacetate (105), acid bromate (106) and hexacyanoferrate (III) in alkaline medium (107).

PRESENT WORK

The present work is a detailed kinetic investigation of the oxidation of aromatic amines by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, using aqueous methanol (v/v) as solvent. The aromatic amines which have been used for the purposes of oxidation have included:

(a) Aniline and substituted anilines

(b) N-Methylaniline; N-ethylaniline; diphenylamine and substituted diphenylamines

(c) N,N-Dimethylaniline; N,N-diethylaniline.

(d) Benzylamine and substituted benzylamines

Stoichiometry (Vide 'Experimental'):

The stoichiometry of the reactions were determined to be:

(a) For aniline

$$2Ar\,NH_2 + 4Fe(CN)_6^{3-} \longrightarrow ArN{=}NAr + 4Fe(CN)_6^{4-} + 4H^+ \quad .$$

(b) For N-methylaniline

$$C_7H_9N + 4Fe(CN)_6^{3-} + H_2O \longrightarrow C_7H_7NO + 4Fe(CN)_6^{4-} + 4H^+ \quad .$$

(c) For N-ethylaniline

$$C_8H_{11}N + 6Fe(CN)_6^{3-} + 2H_2O \longrightarrow C_7H_7NO + CH_2O + 6Fe(CN)_6^{4-} + 6H^+ .$$

(d) For diphenylamine

$$2C_{12}H_{11}N + 2Fe(CN)_6^{3-} \longrightarrow C_{24}H_{20}N_2 + 2Fe(CN)_6^{4-} + 2H^+ .$$

(e) For N,N-dimethylaniline

$$C_8H_{11}N + 4Fe(CN)_6^{3-} + H_2O \longrightarrow C_8H_9NO + 4Fe(CN)_6^{4-} + 4H^+$$

(f) For N,N-diethylaniline

$$C_{10}H_{15}N + 8Fe(CN)_6^{3-} + 3H_2O \longrightarrow C_7H_7NO + CH_2O + C_2H_4O + 8Fe(CN)_6^{4-} + 8H^+ .$$

(g) For benzylamine

$$C_7H_9N + 2Fe(CN)_6^{3} + H_2O \longrightarrow C_7H_6O + 2Fe(CN)_6^{4-} + NH_3 + 2H^+ .$$

Effect of substrate and oxidant

The rates of all these oxidation reactions were dependent on the first powers of the concentrations of substrate and oxidant (Tables 1-5).

Table 1: Effect of substrate and oxidant

/ Aniline / (10^2 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^4 x k_{obs} (s^{-1})
1.0	1.0	1.9
5.0	1.0	9.6
10.0	1.0	19.5
25.0	1.0	48.3
1.0	0.5	1.8
1.0	0.25	1.8
1.0	0.10	1.9

/ NaOH / = 2.5×10^{-3} M; μ = 0.1M ;

MeOH = 30% (v/v) ; temp. = 35°C.

Table 2 : Effect of substrate and oxidant

/ Substrate / (10^2 x M)	/ $K_3Fe(CN)_6$ / 10^3 x M	10^5 x k_{obs} (s^{-1}) N-methyl-aniline	N-ethyl-aniline
1.0	1.0	6.0	7.5
2.5	1.0	15.0	19.0
5.0	1.0	30.0	38.0
10.0	1.0	61.0	75.0
25.0	1.0	150.0	190.0
1.0	0.75	6.3	7.8
1.0	0.50	6.5	7.2
1.0	0.25	6.5	7.5
1.0	0.10	6.0	7.6

/ NaOH / = 1 x 10^{-2}M; μ = 0.25M; MeOH = 60% (v/v); temp. = 35°C.

Teble 3: Effect of substrate and oxidant

/ Substrate / (10^2 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^5 x k_{obs} (s^{-1}) N,N-dimethyl-aniline	N,N-diethyl-aniline
1.0	1.0	9.5	11.5
2.5	1.0	24.0	29.0
5.0	1.0	48.0	60.0
10.0	1.0	96.0	121.0
25.0	1.0	245.0	290.0
1.0	0.75	9.5	11.6
1.0	0.50	9.3	11.5
1.0	0.25	9.6	11.2
1.0	0.10	9.5	11.3

/NaOH / = 1x10^{-2}M; μ = 0.25M; MeOH = 60% (v/v); temp. = 35°C.

Table 4: Effect of substrate and oxidant

/ Diphenylamine / (10^2 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^5 x k_{obs} (s^{-1})
1.0	1.0	5.5
2.5	1.0	13.5
5.0	1.0	28.0
10.0	1.0	55.0
25.0	1.0	138.0
1.0	0.75	5.8
1.0	0.5	5.6
1.0	0.25	5.0
1.0	0.1	5.6

/ NaOH / = 0.1M; μ = 0.1M; MeOH = 70% (v/v); temp. = 50°C.

Table 5: Effect of substrate and oxidant

/ Benzylamine / (M)	/ $K_3Fe(CN)_6$ / (10^2 x M)	10^6 x k_{obs} (s^{-1})
0.1	1.0	7.0
0.25	1.0	17.0
0.50	1.0	35.0
1.0	1.0	69.0
2.5	1.0	170.0
1.0	2.5	68.0
1.0	5.0	70.0
1.0	10.0	68.0

/ NaOH / = 1 x 10^{-2}M; μ = 0.1 M;

MeOH = 60% (v/v); temp. = 60°C.

Plots of k_{obs}, the pseudo-first order rate constant, against a 25-fold range of concentration of substrates, gave straight lines passing through the origin, indicating that the rate of oxidation was dependent on the first power of the concentrations of the substrates. This was further seen by the constant values of k_2, the second order rate constant. When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant (10-fold range), indicating a first order dependence of the reaction on the concentration of the oxidant (Tables 1-5).

Effect of alkali

The rate of the reaction was independent of the concentration of alkali in the range studied (Tables 6-10).

Table 6 : Effect of alkali

/ NaOH / (10^3 x M)	10^4 x k_{obs} (s^{-1})
2.5	1.9
5.0	1.9
10.0	1.8
25.0	1.8

/ Aniline / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; μ = 0.1 M; MeOH = 30%(v/v); temp. = 35°C.

Table 7: Effect of alkali

/ NaOH / (10^2 x M)	10^5 x k_{obs} (s^{-1}) N-methyl-aniline	N-ethyl-aniline
1.0	6.0	7.5
2.5	6.0	7.5
5.0	6.5	7.8
10.0	6.3	7.5
25.0	6.0	7.5

/ Substrates / = 1×10^{-2}M; / $K_3Fe(CN)_6$ / = 1×10^{-3} M;

μ = 0.25 M; MeOH = 60%(v/v); temp. = 35°C.

Table 8: Effect of alkali

/ NaOH / (10^2 x M)	10^5 x k_{obs} (s^{-1}) N,N-dimethyl-aniline	N,N-diethyl-aniline
1.0	9.5	11.5
2.5	9.5	11.6
5.0	9.3	11.5
10.0	9.5	11.2
25.0	9.6	11.3

/ Substrates / = 1×10^{-2}M; / $K_3Fe(CN)_6$ / = 1×10^{-3}M;

μ = 0.25M; MeOH = 60% (v/v); temp. = 35°C.

Table 9: Effect of alkali

/ NaOH / (10^2 x M)	10^5 x k_{obs} (s^{-1})
1.0	5.5
2.5	5.2
5.0	5.0
10.0	5.5
25.0	5.5

/ Diphenylamine / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3}M;

μ = 0.25 M; MeOH = 70% (v/v); temp. = 50°C.

Table 10: Effect of alkali

/ NaOH / (10^2 x M)	10^6 x k_{obs} (s^{-1})
1.0	69.0
2.5	68.0
5.0	70.0
10.0	67.0
25.0	68.0

/ Benzylamine / = 1.0 M; / $K_3Fe(CN)_6$ / = 1 x 10^{-2}M;

μ = 0.1M; MeOH = 60% (v/v); temp. = 60°C.

The oxidation of all these amines was also possible with neutral hexacyanoferrate (III), but the reactions were very slow. This showed that an alkaline medium was necessary for the facile oxidation of these amines. Though there was no dependence on alkali over the concentration range studied, the rate was not independent of the concentration of alkali in the wider sense.

Rate law

Under the present experimental conditions, the rate law could be expressed as :

$$\text{Rate} = - \frac{d/Fe(CN)_6^{3-}/}{dt} = k_{obs} / \text{Amine} / / Fe(CN)_6^{3-} / \quad \ldots\ldots \quad (1)$$

The pseudo-first order rate constant, k_{obs}, was calculated from the equation (108):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \quad \ldots \quad \ldots \quad (2)$$

(vide 'Experimental': Calculations).

Effect of solvent

Reactions involving an ionic reactant are susceptible to solvent influences. It is hence to be expected that in the present investigation, the solvent should be playing an important role. The oxidation of amines is definitely influenced by the solvent system. The rate of oxidation was slowest in those solvent mixtures that

contained the largest proportions of water, and increasing proportions of methanol resulted in an increase in the rate of oxidation (Tables 11-12). In the case of the oxidation of N,N-dimethylaniline, increasing proportions of methanol resulted in a decrease in the rate of oxidation (Table 13).

Table 11: Effect of solvent

MeOH - H_2O (%, v/v)	$10^4 \times k_{obs}$ (s^{-1})
30-70	1.9
35-65	3.1
40-60	5.0
45-55	8.9
50-50	15.1

/ Aniline / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3} M;

/ NaOH / = 2.5 x 10^{-3} M; μ = 0.1M; temp. = 35°C.

Table 12: Effect of solvent

MeOH-H_2O (%, v/v)	10^5 x k_{obs} (s^{-1})
55-45	4.0
60-40	4.3
65-35	4.8
70-30	5.5

/ Diphenylamine / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; / NaOH / = 0.1M; μ = 0.1 M; temp. = 50°C.

Table 13: Effect of solvent

MeOH-H_2O (%, v/v)	10^5 x k_{obs} (s^{-1})
45-55	18.2
50-50	15.2
55-45	12.5
60-40	9.5
65-35	7.3

/ N,N-dimethylaniline / = 1x10^{-2}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; / NaOH / = 1 x 10^{-2} M; μ = 0.25 M; temp. = 35°C.

In the present investigation, in going from lower to higher percentages of methanol (v/v), the polarity decreases. This decrease in the polarity of the medium caused an increase in the rate of the reaction (Tables 11-12). A plot of log k_{obs} against the reciprocal of the dielectric constant was linear (Figs. 1-3), indicating that the reactions under consideration were of the ion-dipole type (109).

A complete explanation of the role of the solvent in chemical reactions cannot be offered on the basis of the dielectric constant of the medium alone.

On the basis of the solvating power of the solvent, a correct prediction of a qualitative nature can be made of the rate of the reaction in different solvent media. In the present investigation, the transition state is less polar than the initial state (reactants), because of the increased dispersal of charges in the transition state. This would indicate that the extent of solvation of the transition state was less than that for the reactants, thus agreeing with the assumptions of Hughes and Ingold (110). Therefore, the decrease in the rate of oxidation on the addition of a more polar solvent (Tables 11-12), in the present work, is a natural result of the progressive increase in solvation of the reactants more than that of the transition state.

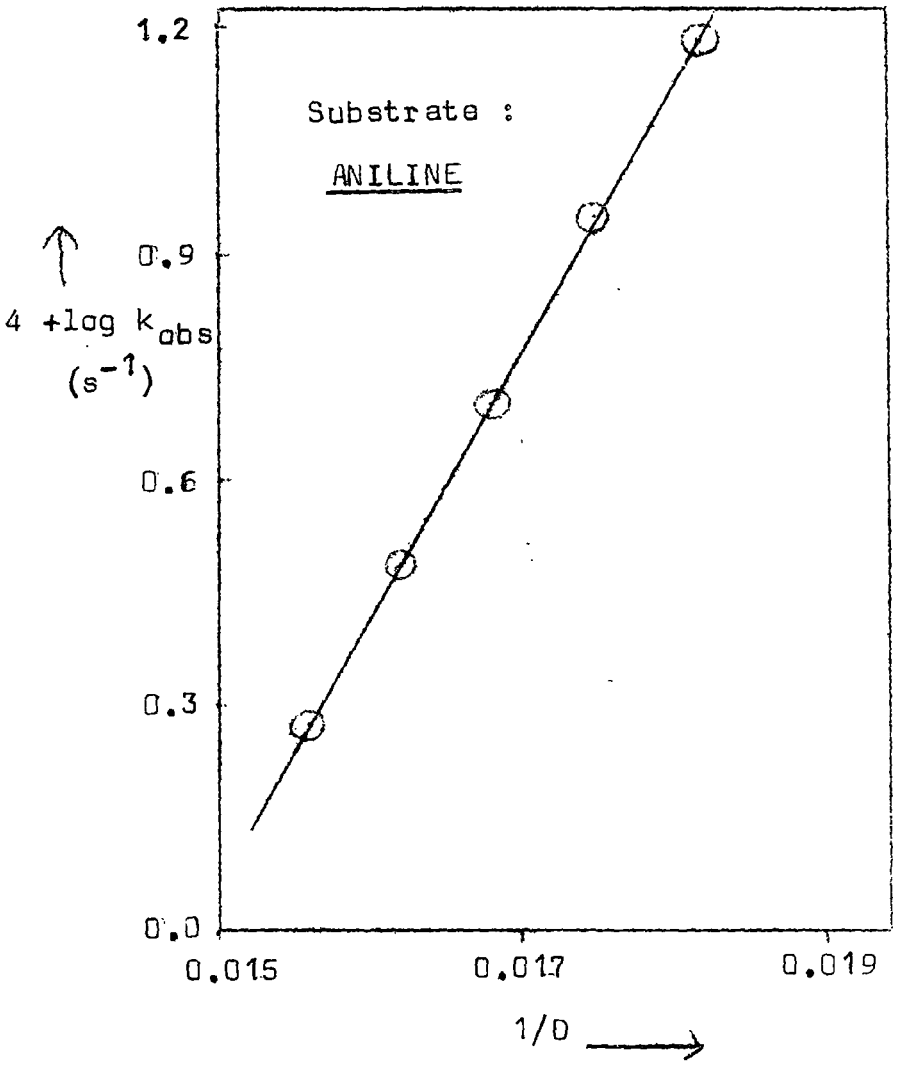


Fig. 1 . Plot of log k_{obs} against the reciprocal of the dielectric constant (Substrate: ANILINE).

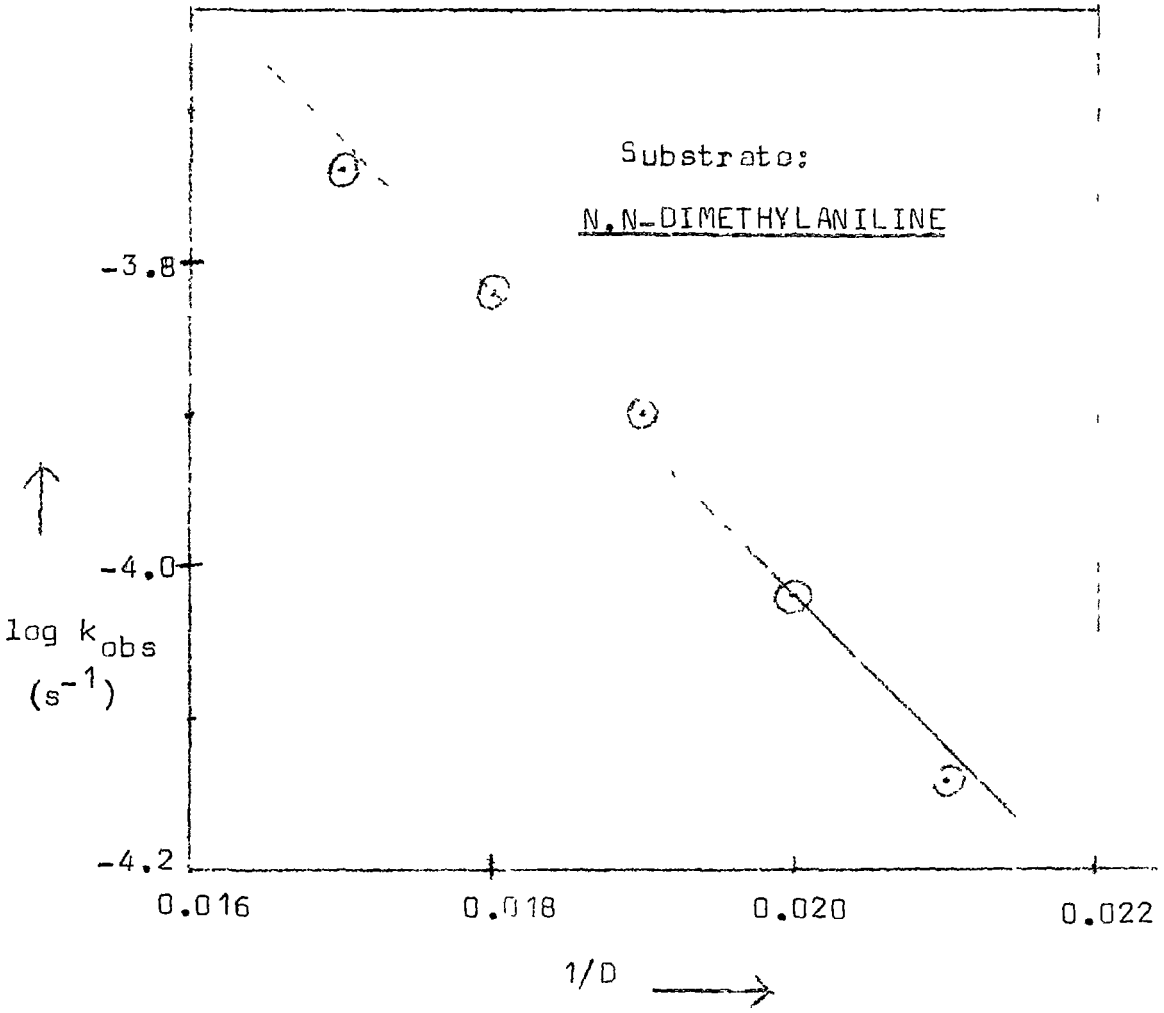


Fig. 2 . Plot of log k_{obs} against the reciprocal of the dielectric constant (Substrate : N,N-DIMETHYLANILINE)

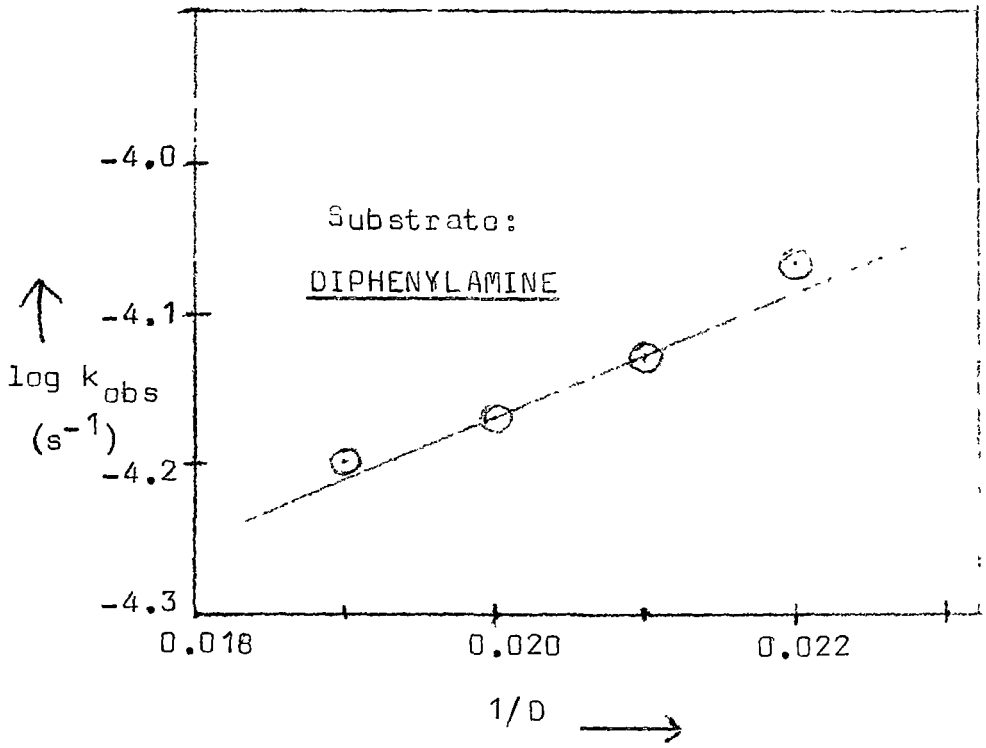


Fig. 3 . Plot of log k_{obs} against the reciprocal of the dielectric constant (Substrate : DIPHENYLAMINE)

The effect of a change in the solvent composition on reaction rates would also depend on factors such as solvent - solute interactions (111, 112), and on solvent structure (109).

Effect of temperature

The rate of the reaction was influenced by changes in temperature, the rate showing an increase with an increase in the temperature (Tables 14 - 18).

Table 14: Effect of temperature

Temp.($\pm$0.1°C)	$10^4 \times k_{obs}$ (s^{-1})
35.0	1.9
45.0	3.1
50.0	4.1
60.0	6.4

/ Aniline / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3} M;

/ NaOH / = 2.5 x 10^{-3} M; aq. methanol = 30% (v/v);

μ = 0.1 M.

Table 15: Effect of temperature

Temp. ($\pm$ 0.1°C)	$10^5 \times k_{obs}$ (s^{-1})	
	N-methyl-aniline	N-ethyl-aniline
30.0	4.4	6.0
35.0	6.0	7.5
40.0	8.5	9.5
45.0	11.1	12.6
50.0	14.0	15.5

/ Substrates / = 1 x 10^{-2} M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3} M;

/ NaOH / = 1 x 10^{-2}M; aq. methanol = 60%(v/v); μ = 0.25M.

Table 16: Effect of temperature

Temp.($\pm$ 0.1°C)	$10^5 \times k_{obs}$ (s^{-1})	
	N,N-dimethyl-aniline	N,N-diethyl-aniline
30.0	7.2	9.1
35.0	9.5	11.5
40.0	11.8	14.5
45.0	14.3	16.8
50.0	17.2	21.0

/ Substrates / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1x10^{-3} M;

/ NaOH / = 1 x 10^{-2}M; aq. methanol = 60% (v/v);

μ= 0.25 M.

Table 17: Effect of temperature

Temp. ($\pm$ 0.1°C)	$10^5 \times k_{obs}$ (s^{-1})
30.0	0.6
35.0	1.5
40.0	2.6
45.0	3.9
50.0	5.5

/ Diphenylamine / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1x10^{-3} M;

/ NaOH / = 0.1M;aq. methanol = 70% (v/v); μ = 0.1 M.

Table 18: Effect of temperature

Temp. ($\pm$ 0.1°C)	$10^5 \times k_{obs}$ (s^{-1})
50.0	3.7
55.0	5.1
60.0	6.9
65.0	9.1
70.0	11.9

/ Benzylamine / = 1.0 M; / $K_3Fe(CN)_6$ / = 1x10^{-2}M;

/ NaOH / = 1 x 10^{-2} M; aq. methanol = 60%; μ = 0.1 M.

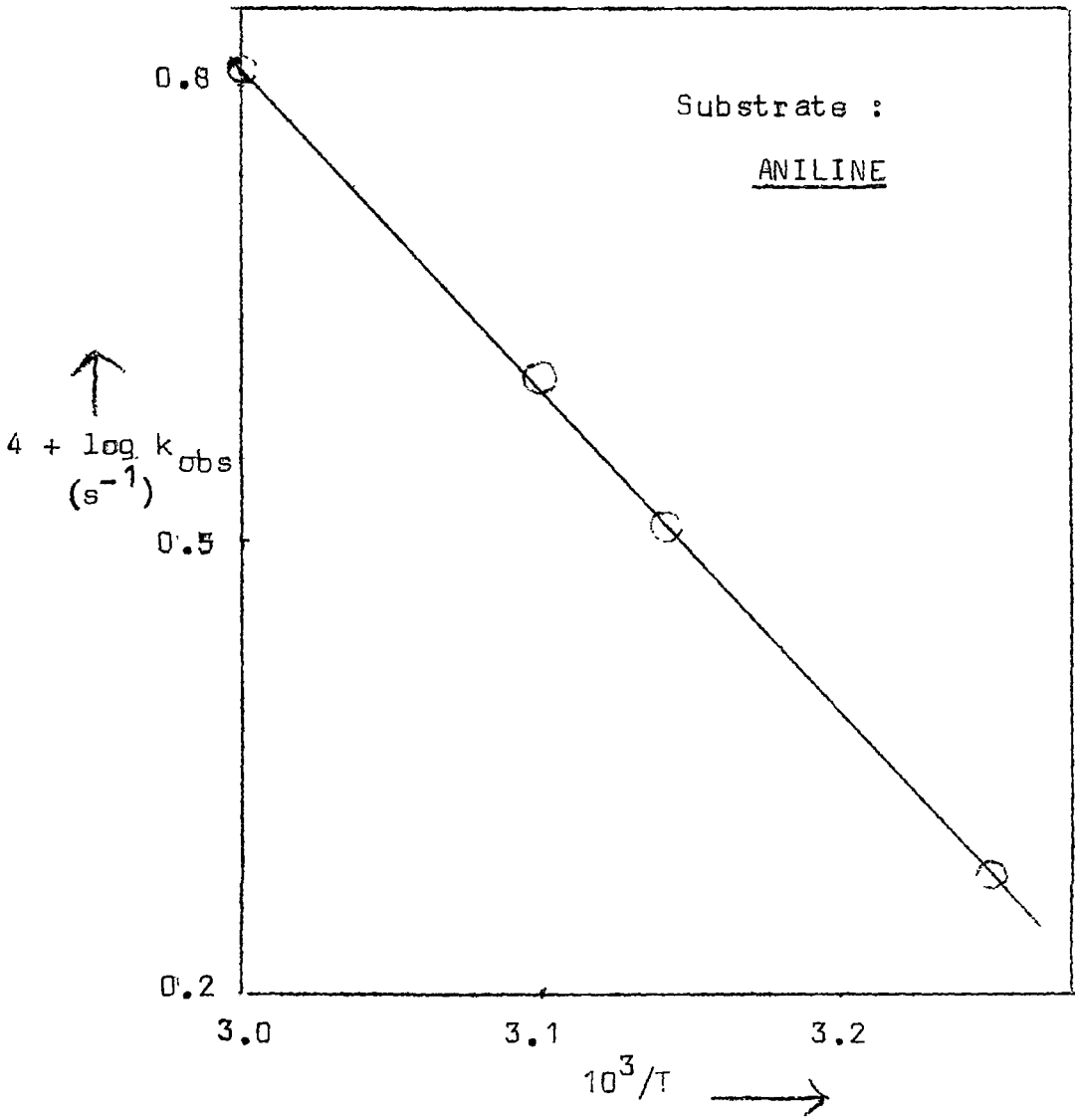


Fig.4. Plot of log k_{obs} against the reciprocal of temperature (Substrate : ANILINE).

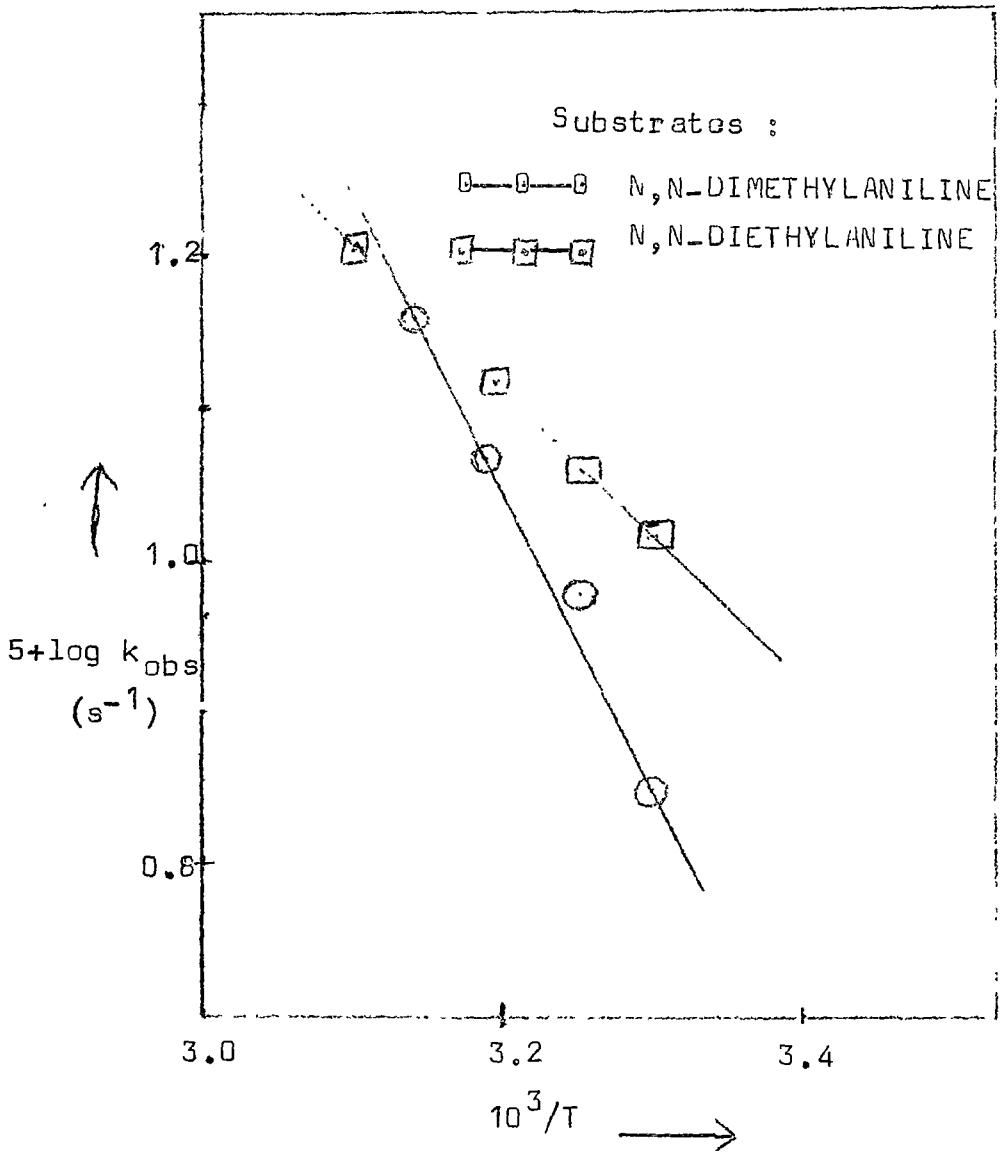


Fig. 5 . Plots of log k_{obs} against the reciprocal of temperature

(Substrates : N,N-DIMETHYL-ANILINE
N,N-DIETHYL-ANILINE)

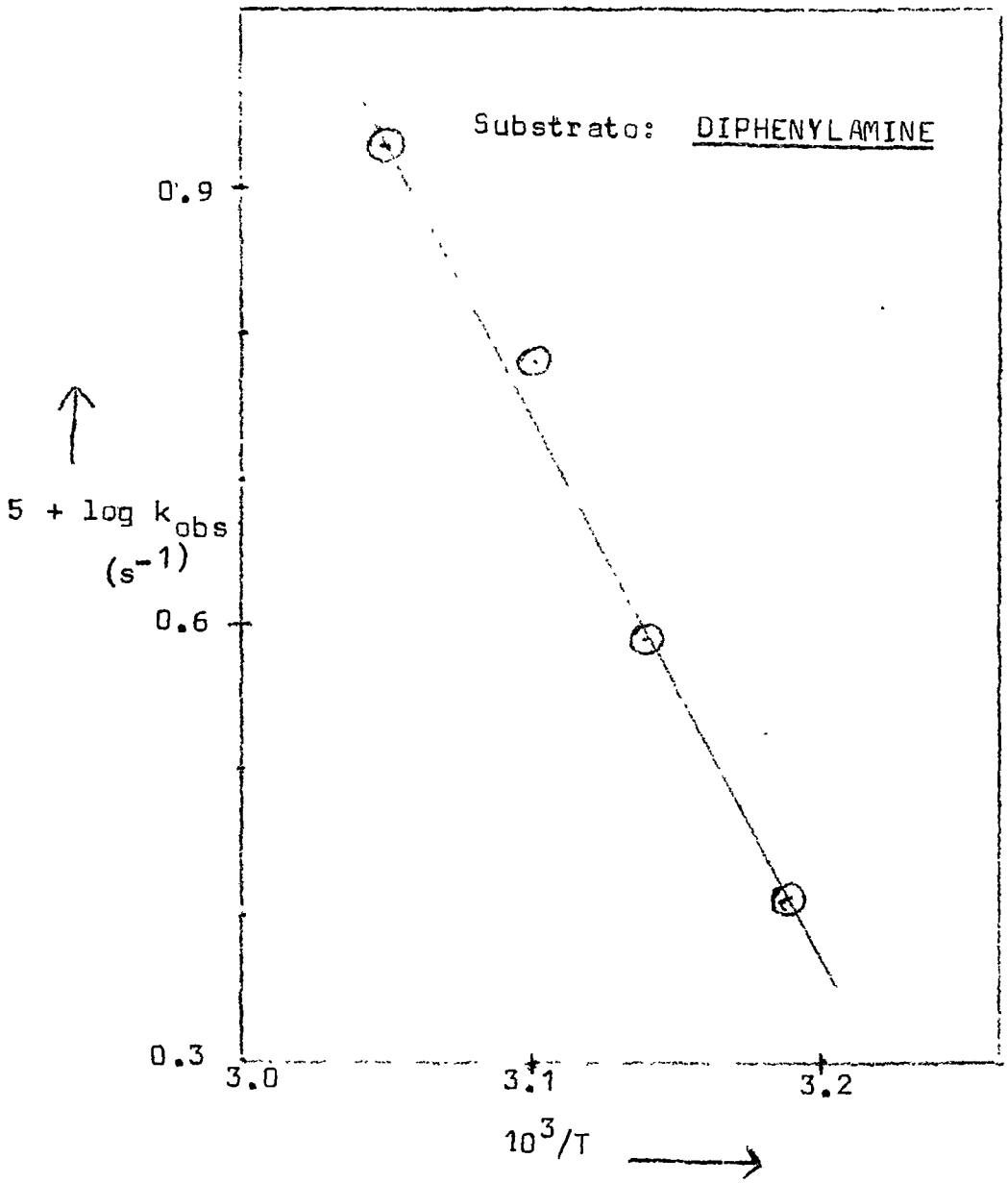


Fig. 6 . Plot of log k_{obs} against the reciprocal of temperature (Substrate : DIPHENYLAMINE)

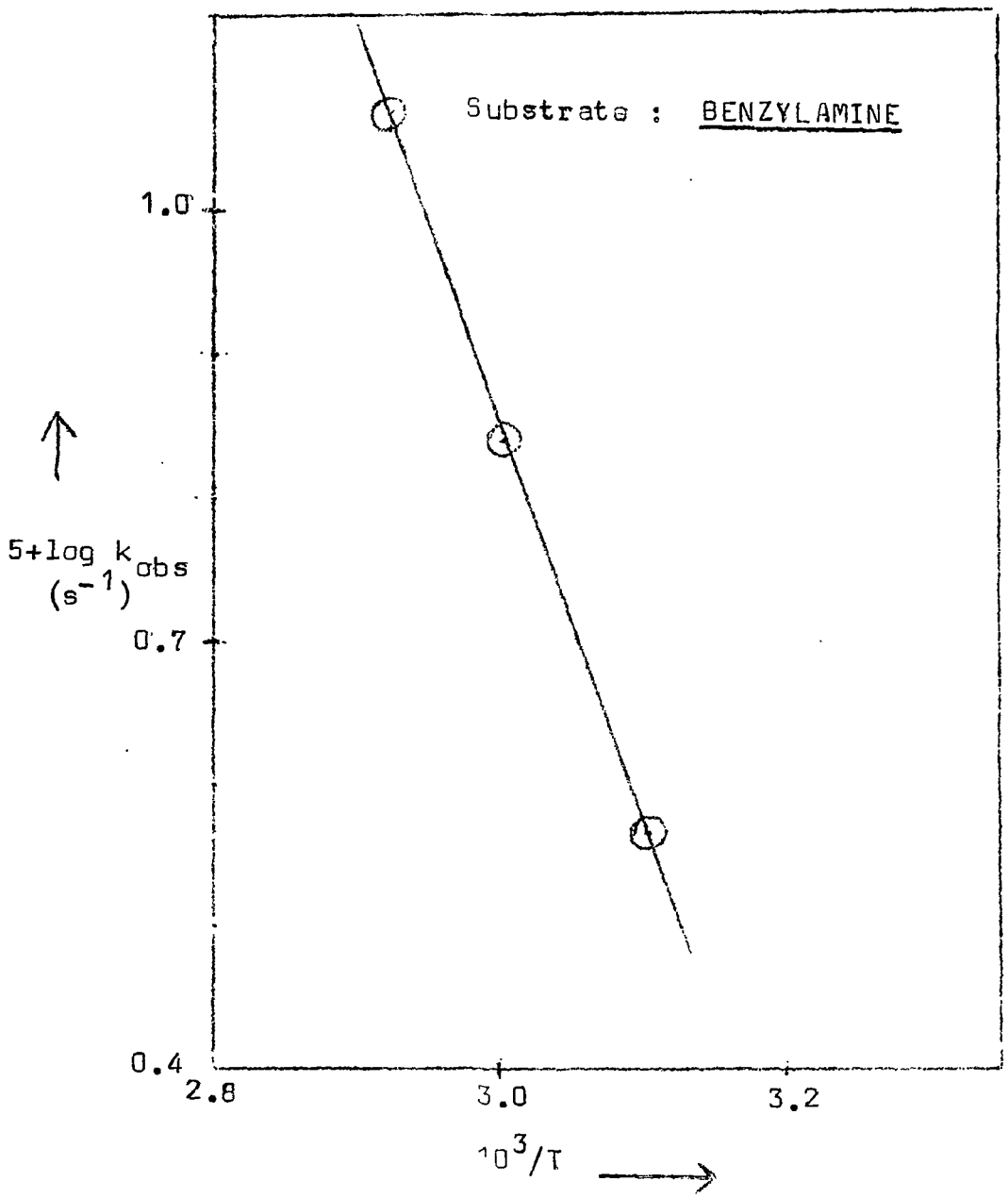


Fig. 7 . Plot of log k_{obs} against the reciprocal of temperature (Substrate : BENZYLAMINE)

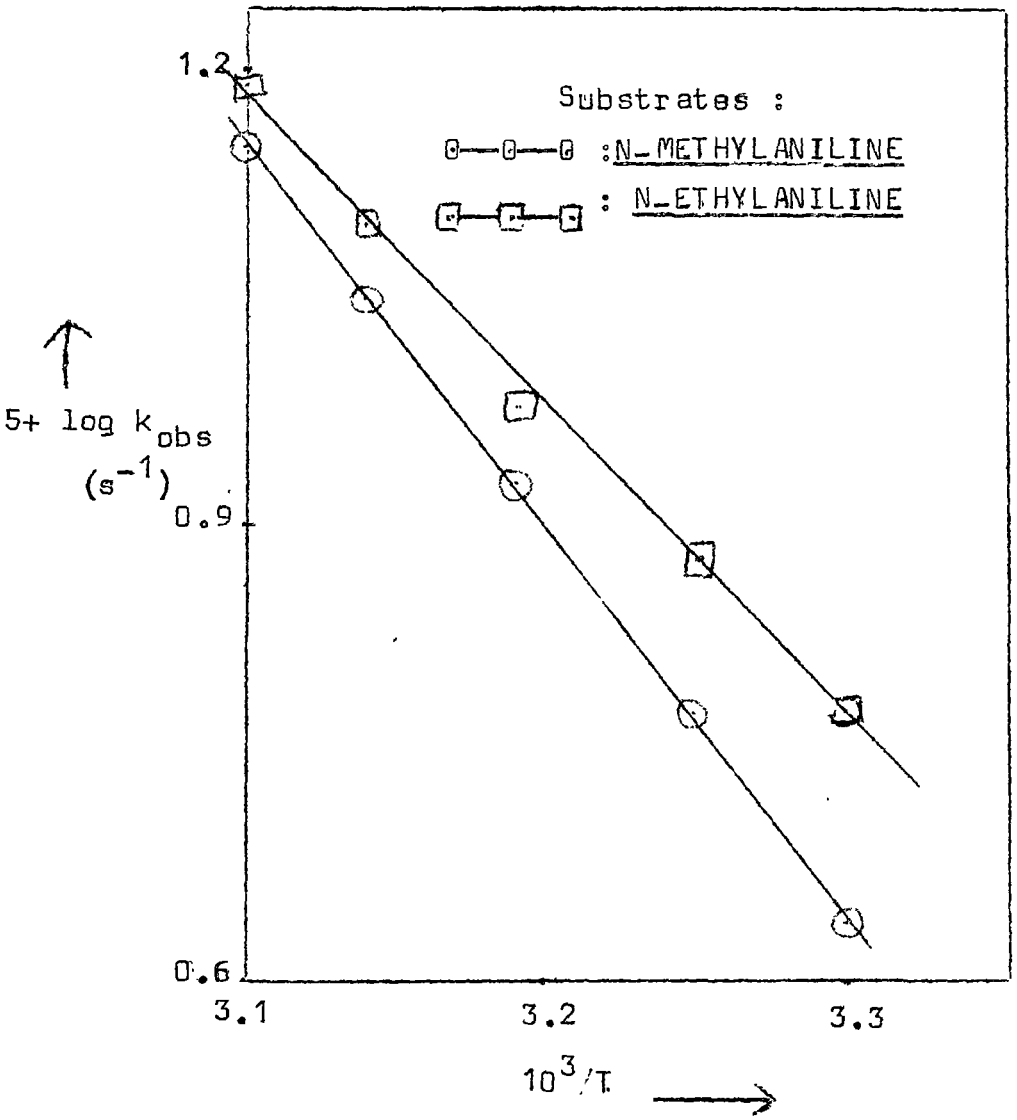


Fig. 8. Plot of log k_{obs} against the reciprocal of temperature

(Substrates: N-METHYL-ANILINE

N-ETHYL-ANILINE)

From the linear plots of log k_{obs} against the reciprocal of temperature (Figs. 4-8), the activation energies were calculated. The other activation parameters have been calculated and are shown in Table 19.

Table 19: Activation Parameters

Substrates	E ($kJ\ mol^{-1}$)	$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	A (s^{-1})	$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)
Aniline	42±2	39±2	$2x10^3$	-190±5
N-Methyl-aniline	42±3	39±3	$8x10^2$	-155±5
N-Ethyl-aniline	40±3	37±3	$5x10^2$	-170±5
N,N-Dimethyl-aniline	36±3	33±3	$1.3x10^2$	-210±6
N,N-Diethyl-aniline	33±3	30±3	$1.5x10^2$	-215±6
Diphenylamine	71±4	68±4	$2x10^7$	-115±5
Benzylamine	53±4	50±4	$2x10^4$	-170±6

The low values of the activation energies and of $\Delta H^{\neq}$ were due to the resonance stabilization of the intermediate radical by the nitrogen lone pair (or the resonance stabilization of the radical cation by the phenyl group). The large negative values of $\Delta S^{\neq}$ suggested that the formation of the transition state was strongly enhanced by entropic factors. Values

of $\Delta S^{\neq}$ in this range for radical reactions have been ascribed (113) to the nature of electron - pairing and electron-unpairing processes, both of which are forbidden processes.

Effect of added $K_4Fe(CN)_6$

The addition of $K_4Fe(CN)_6$ in the concentration range (1.0×10^{-4}M to 1.0×10^{-3}M), did not have any effect on the rates of these oxidation reactions.

Effect of ionic strength

Variations in the ionic strength of the medium using KCl (μ = 0.01 M to 0.25 M), did not have any effect on the rates of these oxidation reactions.

Effect of added salts

The addition of salts such as NaCl, $NaNO_3$, KNO_3, Na_2SO_4, $MgSO_4$ (concentration range 1.0×10^{-4}M to 5.0×10^{-3}M), did not have any effect on the rates of these oxidation reactions.

Structural influences on the rate of oxidation

The introduction of electron releasing groups caused an increase in the rate of the reaction, whereas electron withdrawing groups caused a decrease in the rate of

the reaction. Such structural effects have been observed in the case of aniline and substituted anilines (Table 20), diphenylamine and substituted diphenylamines (Table 21), and for benzylamine and substituted benzylamines (Table 22).

Table 20: Effect of substituents (anilines)

/ Substituent / (0.01 M)	$10^5 \times k_{obs}$ (s^{-1})
p-methoxy	105.0
o-methoxy	43.0
p-methyl	38.0
o-methyl	27.0
m-methyl	22.0
H(aniline)	19.0
p-chloro	15.0
o-chloro	12.0
m-chloro	8.0
m-nitro	4.0
p-nitro	3.0
o-nitro	2.0

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; / NaOH / = 2.5 x 10^{-3}M;

aq. methanol = 30% (v/v); μ = 0.1M; temp. = 35°C.

Table 21: Effect of substituents (diphenylamines)

/ Substituents / (0.01M)	10^5 x k_{obs} (s^{-1})
p-amino	25.1
p-methoxy	10.0
p-methyl	7.1
H(diphenylamine)	5.5
m-nitro	1.1
p-nitro	0.9

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; / NaOH / = 0.1 M;

aq. methanol = 70% (v/v); μ = 0.1M; temp. = 50°C.

Table 22: Effect of substituents (benzylamines)

/ Substituent / (1.0M)	10^6 x k_{obs} (s^{-1}).
p-methoxy	412
p-methyl	148
m-methyl	83
H(benzylamine)	69
m-methoxy	62
p-chloro	54
m-chloro	28
m-nitro	15
p-nitro	11

/ $K_3Fe(CN)_6$ / = 0.01 M; / NaOH / = 1x10^{-2}M;

aq. methanol = 60% (v/v); μ = 0.1M; temp. = 60°C.

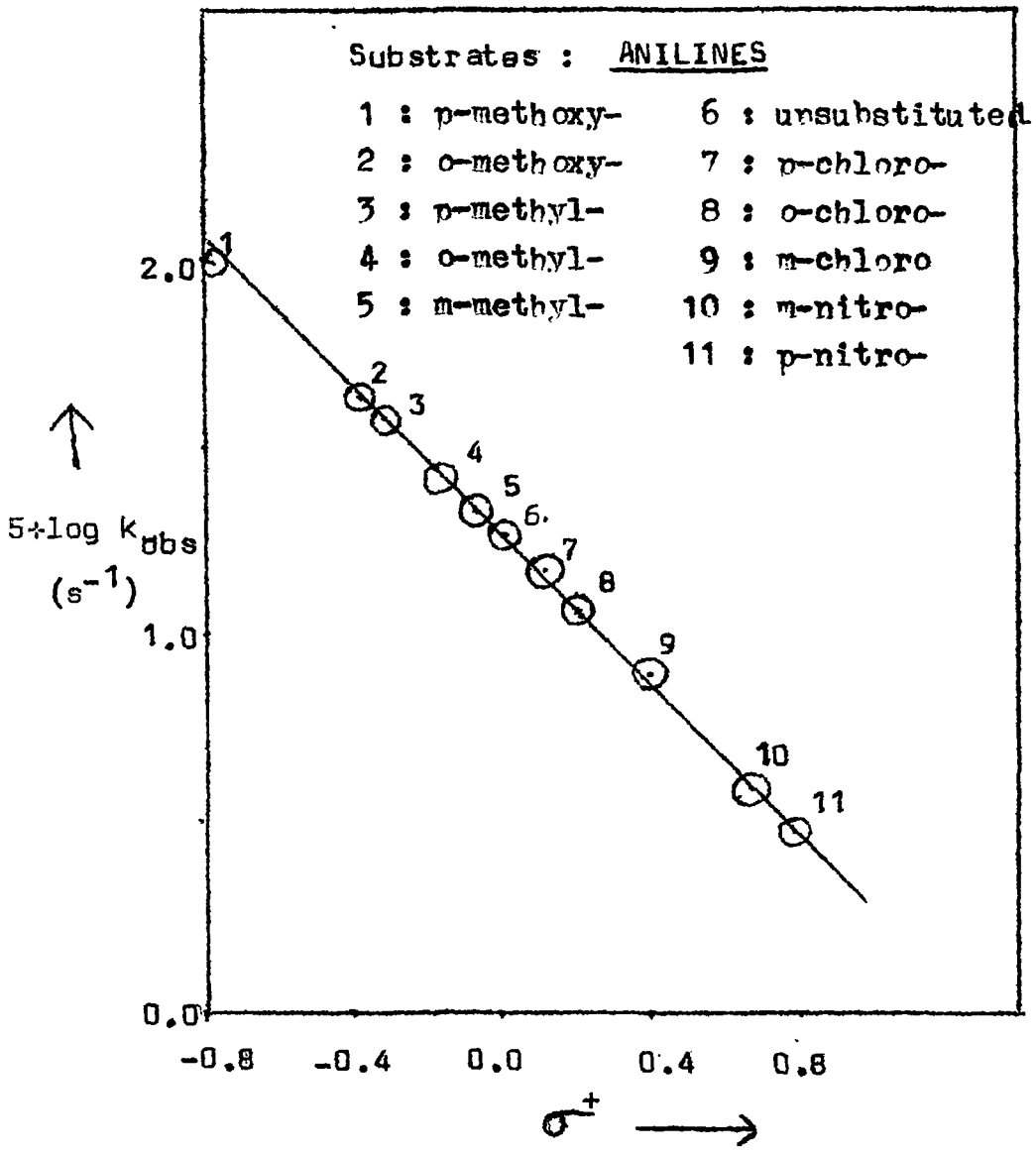


Fig. 9 Plot of log k_{obs} against σ^+

(Substrates: ANILINE and SUBSTITUTED ANILINES)

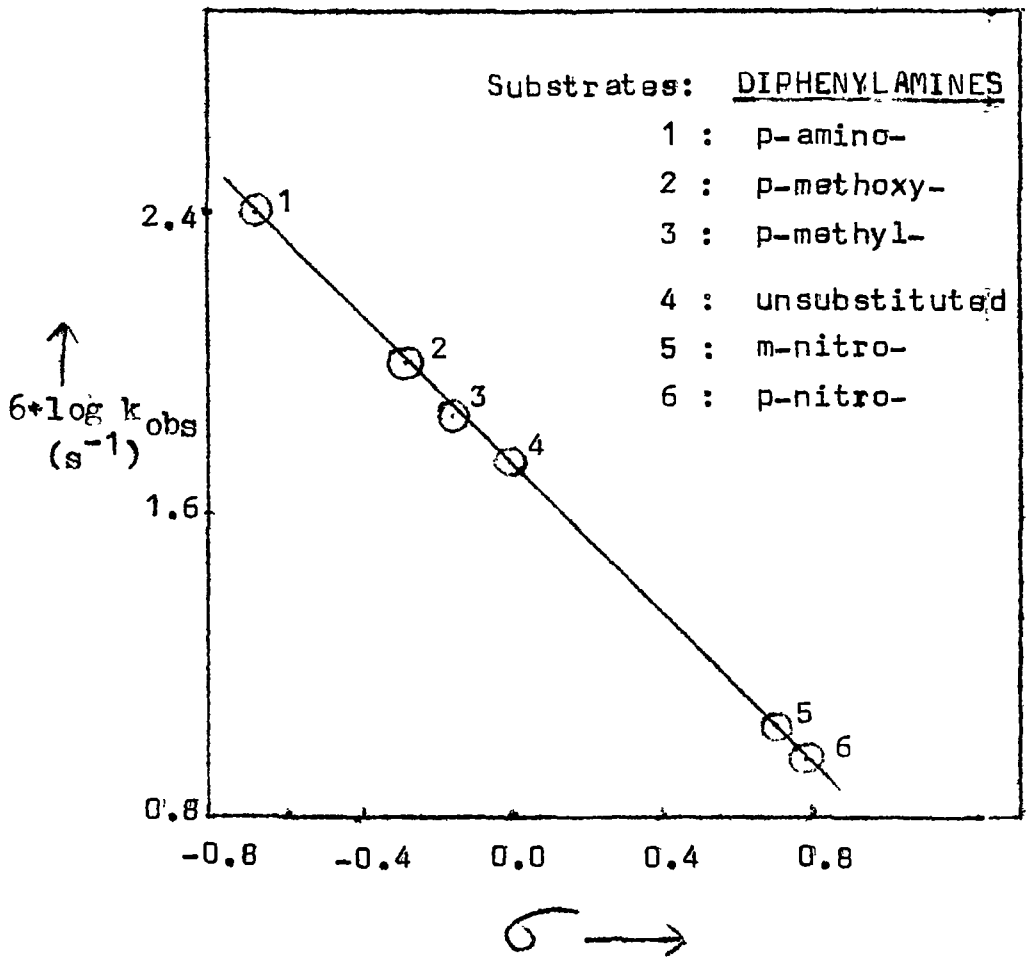


Fig.10 Plot of log k_{obs} against σ

(Substrates: DIPHENYLAMINE and SUBSTITUTED DIPHENYLAMINES).

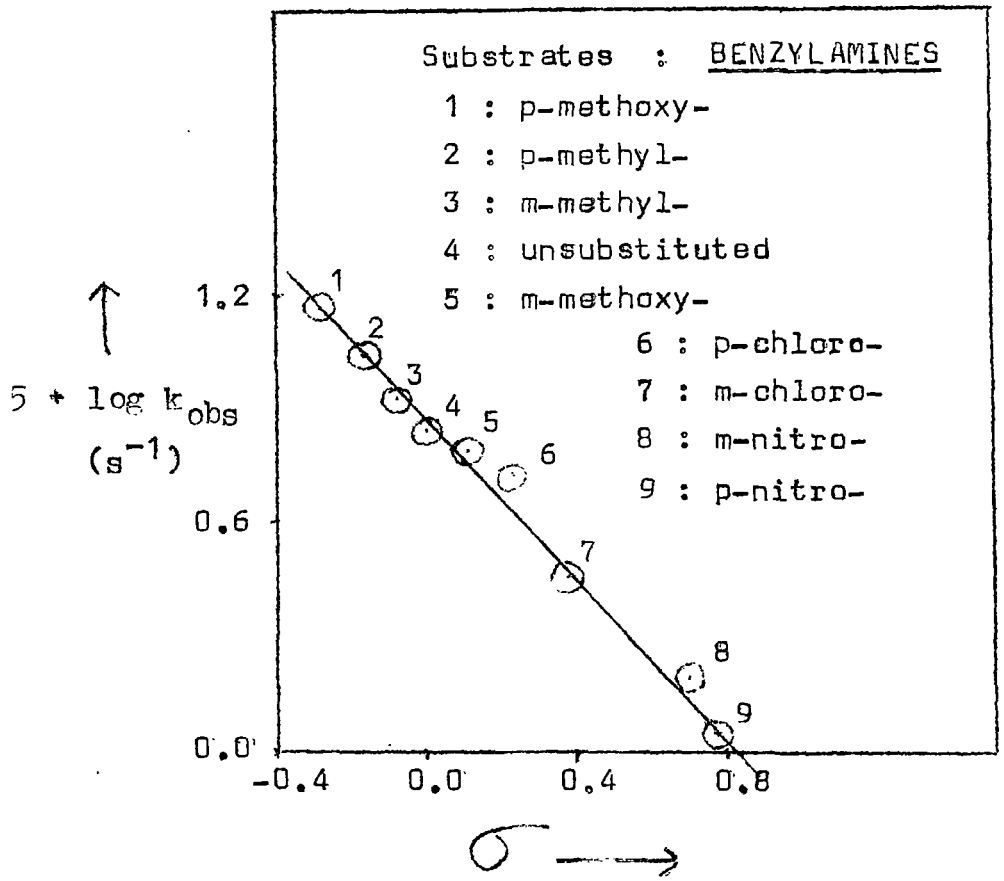


Fig.)1 Plot of log k_{obs} against σ
(Substrates : BENZYLAMINE and
SUBSTITUTED BENZYLAMINES)

Hammett plot

Plots of log k_{obs} against σ^+ (or σ) were linear (Figs. 9-11), and the slopes gave ρ^+ (or ρ) values (correlation coefficient = 0.99 in each case) as shown in Table 23.

Table 23* : Values of ρ^+ (or ρ)

Substrates	ρ^+ (or ρ)
Anilines	- 1.0 (ρ^+)
Diphenylamines	- 1.0 (ρ)
Benzylamines	- 1.0 (ρ)

* Values of σ^+ , σ , and σ_o have been taken from ref.114.

Values of ρ between - 0.75 and - 1.8 indicate radical processes (115,116), whereas the formation of an ionic intermediate would yield values of ρ between - 3.0 and -5.0 (117-119). In the present investigation, the ρ values for these substrates (anilines, diphenylamines and benzylamines) were in the range for processes wherein the rate determining step involved the formation of radical intermediates.

Polymerization of acrylonitrile and precipitation with mercuric chloride have been observed in these amine oxidation reactions, supporting the formation of radical intermediates in the rate determining step.

Kinetic isotope effect

The Oxidation of benzylamine α- d_2 exhibited a kinetic isotope effect, with $k_H / k_D = 6.3$, indicating a cleavage of the C-H bond of the methylene group attached to the aryl ring. This would result in the formation of a radical intermediate. In the oxidation of organic substrates, similar k_H / k_D values had indicated a cleavage of the C-H bond, giving a radical intermediate (116,120-122).

Radical Intermediates

The esr spectra of the corresponding radicals, generated from the oxidation of the substrates, were obtained (vide 'Experimental' : ESR measurements).

(a) From the oxidation of aniline

The esr spectrum of the radical, generated from the oxidation of aniline, contained 4 sets of 1:2:1 triplets. This splitting pattern was attributed to the interaction of the unpaired electron spin with the nitrogen atom, the hydrogen atom attached to the nitrogen, and the two hydrogen atoms at positions ortho to the nitrogen atom. This spectrum was similar to that of the short-lived anilino radical ($C_6H_5\dot{N}H$), observed during the flash photolysis of aniline in the gas phase (123), or by continuous irradiation in rigid glasses (124).

(b) From the oxidation of diphenylamine

The esr spectrum of the radical, generated from the oxidation of diphenylamine, gave a 1:2:1 triplet, corresponding to the diphenylamino radical ($Ar_2\dot{N}$). The coupling constants (in gauss) for the diphenylamino radical were; a_N = 8.85, a_H (ortho) = 3.68, a_H (meta) = 1.50, a_H (para) = 4.30, with a value of g_{av} = 2.0030 ± 0.0002.

(c) From the oxidation of N,N-dimethylaniline

The esr spectrum of the radical, generated from the oxidation of N,N-dimethylaniline, gave 3 spectral lines with peak heights of 1:2:1. This is the peak height distribution for an unpaired electron in the environment of two equivalent hydrogen atoms. The following inferences can be drawn from this spectrum:

(i) the stable radical was formed by the loss of an electron from the nitrogen atom.

(ii) the interaction of the unpaired electron with the methyl groups was not observed, and hence no hyperfine splitting was seen.

(d) From the oxidation of N,N-diethylaniline

The esr spectrum of the radical, generated from the oxidation of N,N-diethylaniline, gave 12 spectral lines. The spectrum indicated that the three protons of the methyl group interact with the unpaired electron to give a hyperfine splitting

of 27.0 gauss. The two methylene protons were magnetically equivalent with a splitting of 22.5 gauss.

(e) From the oxidation of benzylamine

The esr spectrum of the radical, generated from the oxidation of benzylamine, gave 12 spectral lines, consisting of four sets of 1:2:1 triplets. The unpaired electron was subject to an interaction with the nitrogen atom (a_N = 12.0 gauss). The coupling constants (in gauss) were $a_{2,6}$ H = 3.40, $a_{3,5}$ H = 3.45, and a_4H = 3.55.

Mechanism

(a) Oxidation of aniline

The rate of the reaction between aniline and hexacyanoferrate (III) in alkaline medium, was dependent on the first powers of the concentrations of both, substrate and oxidant (Table 1). This indicated that the reaction was directly between the substrate and oxidant.

The addition of hexacyanoferrate (II) ions did not have any effect on the rate of the reaction. This showed that the first step between the substrate and oxidant (the electron abstraction step) was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, indicating that the reaction was between an ion and a neutral (dipolar) species.

The reaction pathway was via the formation of a radical intermediate, characterized as the anilino radical ($ArN\dot{H}$) by ESR spectroscopy as 4 sets of 1:2:1 triplets (vide 'Radical Intermediates').

The formation of the radical intermediate in the rate determining step of the reaction was further supported by the value of $\rho^{+} = -1.0$, which was in the range for reactions proceeding via radical intermediates (115,116).

The subsequent steps, involving oxidative coupling, were rapid, and no intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate hydrazobenzene (A) were not successful. Independent kinetic experiments conducted in this laboratory showed that hydrazobenzene was rapidly converted to azobenzene, under the same experimental conditions. The rate constants at 35°C varied as follows: $10^3 \times k_{obs}(s^{-1}) = 5.5$ (0.01M hydrazobenzene) and 56.0 (0.1M hydrazobenzene), at $[K_3Fe(CN)_6] = 0.001M$ (cf. rate data in Table 1). Thus, hydrazobenzene, if formed as an intermediate in the oxidation of aniline by alkaline hexacyanoferrate(III), would be rapidly oxidized to the product. Earlier work had shown that hydrazobenzene was quartitatively oxidized to azobenzene (8,133), at a much

faster rate than was aniline.

Owing to the ready conversion of aromatic amines to the corresponding arylhydrazines (125), the conversion of monosubstituted hydrazines to their corresponding hydrocarbons appeared to have some synthetic utility (126-132). Symmetrically disubstituted hydrazines such as hydrazobenzene(133), 2,3-diazabicyclo [2.2.1] heptane (135), and 1,1-di-(p-acetamidophenyl) hydrazopropane (136), have been oxidized by copper(II) only as far as the azo compound. Even in the case of some cyclic hydrazines which underwent dehydrogenation to form a hydrazone, rather than an azo compound(137), there was evidence to show that the azo compound may still be an intermediate which underwent rearrangement to the final product.

Primary aromatic amines have been readily oxidized to azobenzenes by cuprous chloride and oxygen, when pyridine was used as the solvent (133, 138-140). The rate of oxidation of aniline to azobenzene was increased by electron donating substituents (133,138).

The presence of an ortho imino group changed the copper (II) oxidation of primary aromatic amines from an intermolecular dimerization to an intramolecular cyclization. Thus acetaldehyde o-aminoanil was cyclized to 2-methylbenzimidazole by cupric acetate (141). An analogous oxidation had occurred in the case of o-aminoazobenzenes (142-146).

The products obtained from the lead tetraacetate oxidation of anilines were best rationalized in terms of intermediate aminium cation radicals ($Ar\overset{+\cdot}{N}H_2$) or anilino radicals ($Ar\dot{N}H$). There was no evidence for the formation of either nitrenes or amino cations, $Ar\overset{+}{N}H$ (147).

It has been established that phenols can undergo oxidative coupling in the presence of oxidizing agents such as ferric chloride (148-150), Fenton's reagent(148-150), manganese trisacetylacetonate in CS_2 or acetonitrile(151), vanadium tetrachloride or vanadium oxytrichloride(152-154), and by hexacyanoferrate(III) in alkaline media(155-161).

In an analogous manner, the oxidative coupling of amines has been effected. With $KMnO_4$ as the oxidant, N-phenyl-2-naphthylamine was converted to the 1,1 -coupling dimer at 0°C in about 40% yield(162). A similar oxidation of N-2-naphthyl-2-naphthylamine by potassium permanganate gave the corresponding carbon-carbon and carbon-nitrogen coupling products in yields of 20% and 30%, respectively (162).

Oxidative coupling, in which a C-C bond or a N-N bond can be generated, was not limited to phenols and aromatic amines. In the oxidation of an olefin with manganic acetate in acetic acid, the major product was a γ-lactone in which acetic acid was coupled oxidatively to the

olefin (163,164). The oxidative coupling of terminal acetylenic compounds to give conjugated diynes has been observed either with cupric acetate in pyridine, or with oxygen, cuprous chloride and ammonium chloride in aqueous ethanol (165-170).

In the present investigation, the mechanism for the oxidation of aniline by alkaline hexacyanoferrate(III) involved the formation of the radical intermediate, which underwent further oxidative coupling to give the product, azobenzene.

The reaction sequence is shown in Scheme 1.

$$Ar\dot{N}H_2 + Fe(CN)_6^{3-} \xrightarrow{slow} Ar\dot{N}H + Fe(CN)_6^{4-} + H^+$$

$$Ar\dot{N}H + ArNH_2 + Fe(CN)_6^{3-} \xrightarrow{fast} \underset{H\ H}{ArN-NAr} + Fe(CN)_6^{4-} + H^+$$

(A)

$$Ar\underset{H}{N}-\underset{H}{N}Ar + 2Fe(CN)_6^{3-} \xrightarrow{fast} ArN=NAr + 2Fe(CN)_6^{4-} + 2H^+$$

(Scheme 1)

The product obtained, azobenzene, was isolated and characterized by spectral methods (vide 'Experimental': Product Analysis).

(b) Oxidation of N-methylaniline

The observation of second order overall kinetics (first order in each, substrate and oxidant) suggests that the reaction involves the direct reaction between the substrate and oxidant (Table 2).

The addition of hexacyanoferrate(II) ions did not have any effect on the rate of the reaction. This showed that the first step of the reaction between the substrate and oxidant (the electron abstraction step) was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, showing that the reaction was between an ion and a neutral (dipolar) molecule.

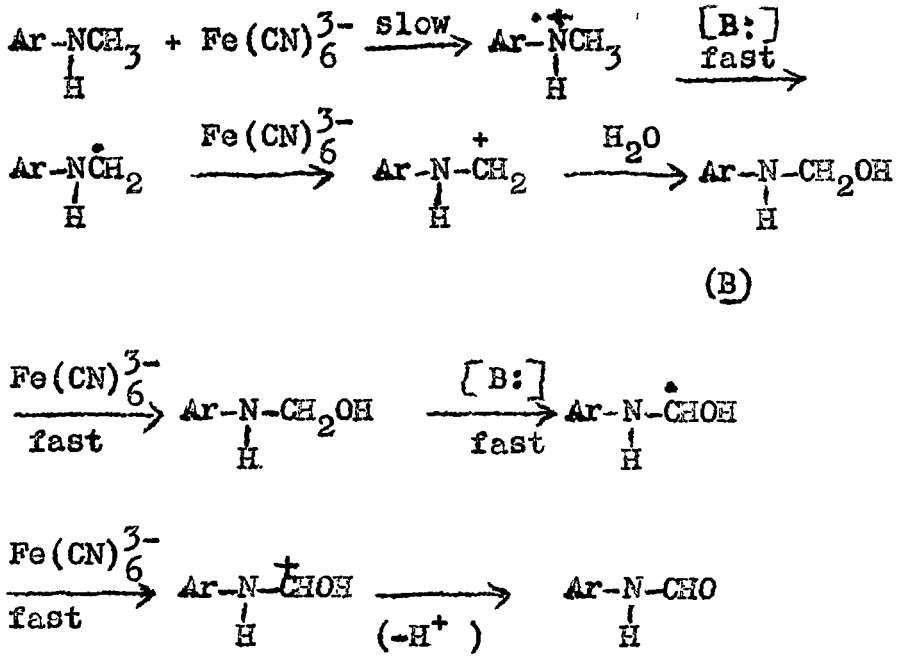
An intermediate free radical was produced by the transfer of one electron, from the nitrogen atom of the amine to the oxidant. The intermediate species was postulated to be an aminium radical cation. Several examples of stable aminium radical cations have been reported (171-182).

The hydrogen abstraction reactions shown in Scheme 2, leading to an intermediate radical species, were two-step reactions. First, the electron was abstracted (rate-limiting), and then the proton was removed by OH^- (fast step). This was the function of the required, but kinetically invisible base.

This mechanism has been demonstrated for a related system (183).

The subsequent steps were rapid, and no intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the carbinolamine (B), were not successful. It could be postulated that the carbinolamine, when formed as an intermediate, would be rapidly converted to the corresponding N-acyl derivative. The mechanism involved the removal of four electrons from the starting compound, which was in agreement with the stoichiometry of the reaction.

The reaction sequence is shown in Scheme 2.



(Scheme 2)

(c) Oxidation of N-ethylaniline

The rate of the reaction was first order in each, substrate and oxidant (Table 2), showing that the rate-determining step involved the direct reaction between the substrate and the oxidant.

The addition of hexacyanoferrate (II) ions did not have any effect on the rate of the reaction. This indicated that the first step of the reaction (electron abstraction step) was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, indicating that the reaction was between an ion and a neutral (dipolar) species.

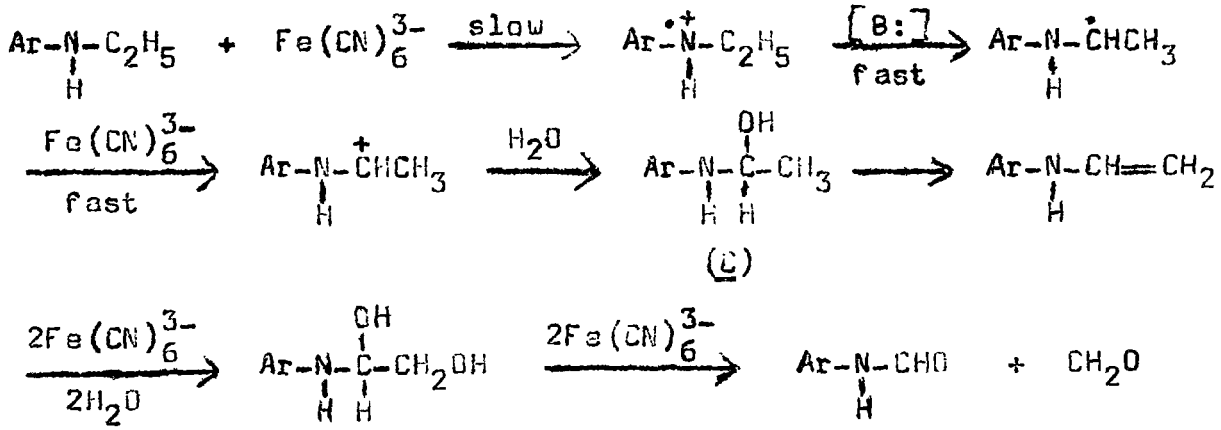
The first step of the reaction involved an electron transfer from the nitrogen atom of the amine to the oxidant, resulting in the formation of the aminium radical cation. Examples of stable aminium radical cations have been reported (171-182).

The hydrogen abstraction reactions shown in Scheme 3, resulting in the formation of intermediate radical species, were two-step reactions. In the first step, the electron was abstracted (slow step). Removal of a proton by the base gave rise to a radical intermediate (fast step). This was the function of the required, but kinetically invisible base. Such a mechanism has been demonstrated for a related system (183).

The subsequent steps were rapid, and no intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the carbinolamine (C), were not successful. The remaining fast steps involved the elimination of water from the carbinolamine, and further oxidation of the resultant enamine to afford an N-acyl derivative (formanilide) and a carbonyl compound (formaldehyde, present as the hydrate). The oxidation of the enamine most likely involved hydroxylation of the double bond followed by oxidative cleavage of the resultant α-glycol, to yield the products. The oxidative cleavage of 1,2-glycols to yield the aldehydes has been established in earlier investigations (184-187).

The mechanism involved the removal of six electrons from the starting compound, which was in agreement with the stoichiometry of the reaction.

The sequence of reactions is shown in Scheme 3.



(Scheme 3)

(d) Oxidation of N, N-Dimethylaniline

The rate of the reaction was first order in each, substrate and oxidant (Table 3), showing that the rate-determining step involved the direct reaction between the substrate and oxidant.

The addition of hexacyanoferrate(II) ions did not have any effect on the rate of the reaction. This indicated that the first step of the reaction (electron abstraction step) was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, showing that the reaction was between an ion and a neutral (dipolar) species.

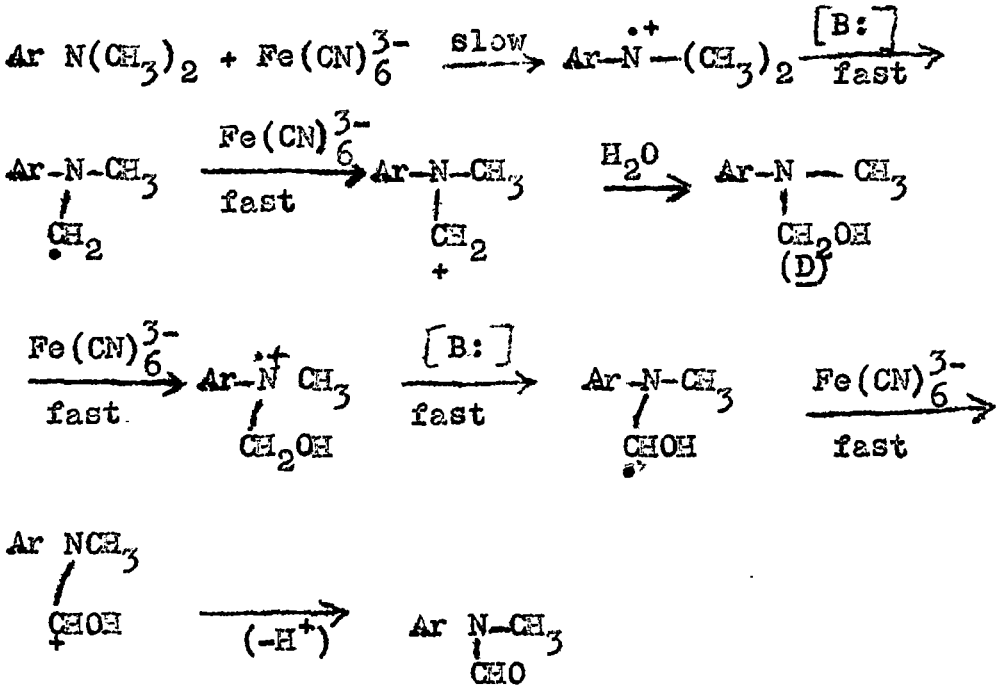
An intermediate free radical was produced by the transfer of one electron, from the nitrogen atom of the amine to the oxidant. The intermediate species was postulated to be an aminium radical cation. Several examples of stable aminium radical cations have been reported (171-182).

The hydrogen abstraction reactions shown in Scheme 4, leading to an intermediate radical species, were two-step reactions. First, the electron was lost(rate-limiting), and

then the proton was abstracted by OH^- (fast step). This was the function of the required, but kinetically invisible base. This mechanism has been demonstrated for a related system (183).

The subsequent steps were rapid, and no intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the carbinolamine(D), were not successful. It could be postulated that the carbinolamine, when formed as an intermediate, would be rapidly converted to the corresponding N-acyl derivative. The mechanism involved the removal of four electrons from the starting compound, which was in agreement with the stoichiometry of the reaction.

The sequence of reactions is shown in Scheme 4.



(Scheme 4).

(e) Oxidation of N,N-diethylaniline

The observation of second order overall Kinetics (first order in each, substrate and oxidant) showed that the mechanistic pathway involved the direct reaction between the substrate and oxidant (Table 3).

The addition of hexacyanoferrate(II) ions did not effect the rate of the reaction, indicating that the first step of the reaction (electron abstraction step) was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, indicating that the reaction was between an ion and a neutral (dipolar) species.

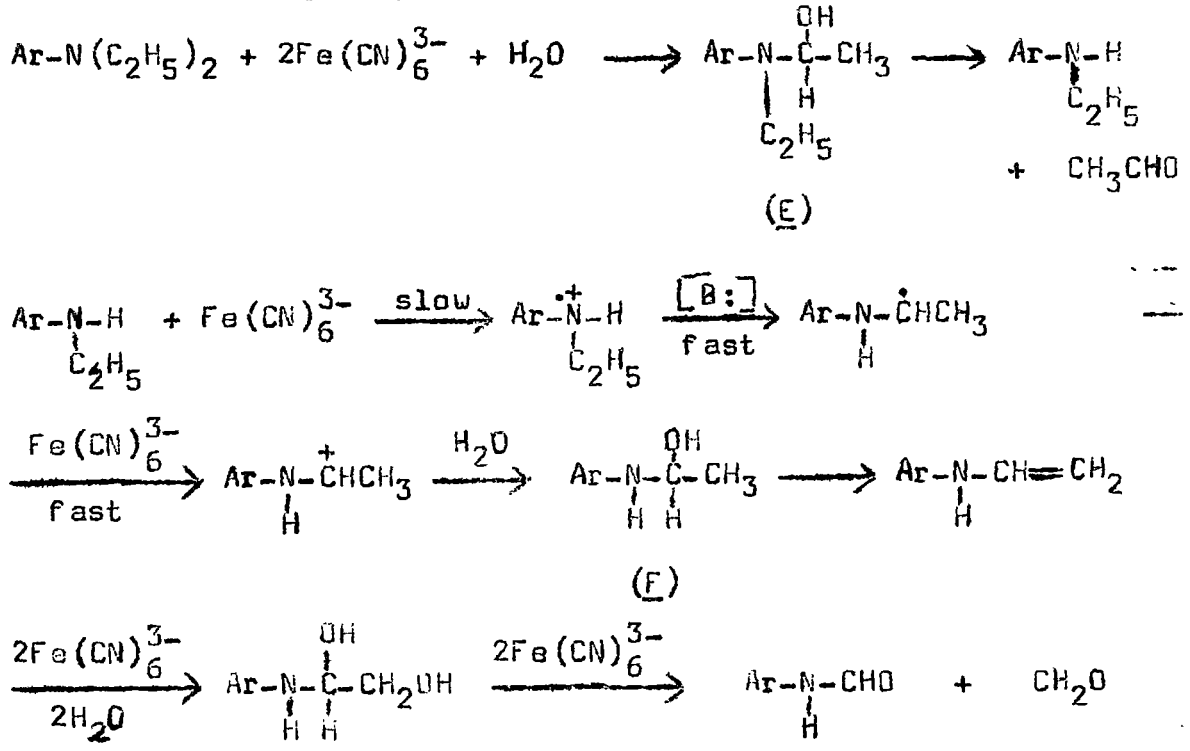
The first step of the reaction involved the oxidation of the amine to the carbinolamine (E), which then underwent rearrangement, rapidly, to give the secondary amine (N-ethylaniline) and acetaldehyde. Evidently, this type of conversion was predominant in the initial stage of the reaction. This would explain the formation of acetaldehyde. The reaction of the secondary amine with the oxidant gave the aminium radical cation (slow step). Removal of the proton by the base gave the radical intermediate (fast step).

The subsequent steps were rapid, and no intermediate product(s) could be isolated from the reaction mixture.

Efforts to isolate the carbinolamine(F), were not successful. The remaining fast steps involved the elimination of water from the carbinolamine, and further oxidation of the resultant enamine to give an N-acyl derivative (formanilide) and a carbonyl compound (formaldehyde, present as the hydrate). The oxidation of the enamine involved the hydroxylation of the double bond, followed by oxidative cleavage of the resultant α-glycol to yield the products. The oxidative cleavage of 1,2-glycols to yield the aldehydes has been established in earlier investigations (184-187).

The mechanism involved the removal of eight electrons from the starting compound, which was in agreement with the stoichiometry of the reaction.

The sequence of reactions is shown in Scheme 5.



(Scheme 5)

The oxidation of N-methylaniline, N-ethylaniline and N,N-diethylaniline to yield formanilide, and the oxidation of N,N-dimethylaniline to yield N-methylformanilide, constitute examples of reactions wherein the oxidation occurred at the N-alkyl side chains, leading to the formation of N-aldehydes.

A significant observation was that while the oxidation of N,N-dimethylaniline by alkaline hexacyanoferrate (III) gave N-methylformanilide (Scheme 4), that is

$$Ar\ N(CH_3)_2 \longrightarrow Ar\ \underset{CH_3}{\overset{|}{N}}CHO ,$$

the alkaline hexacyanoferrate(III) oxidation of N,N-diethylaniline did not give any of the analogous N-ethylacetanilide (Scheme 5), that is

$$Ar\ N(C_2H_5)_2 \not\longrightarrow Ar\text{-}\underset{C_2H_5}{\overset{|}{N}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$$

Instead, the oxidation of N,N-diethylaniline gave formanilide and acetaldehyde (Scheme 5), that is

$$Ar\text{-}N(C_2H_5)_2 \longrightarrow CH_3CHO + Ar\text{-}NH\ C_2H_5$$

$$Ar\text{-}NH\ C_2H_5 \longrightarrow Ar\text{-}NHCH = CH_2 + Ar\text{-}\underset{H}{N}\text{-}CHO$$

Evidently, in the oxidation of N,N-diethylaniline by alkaline hexacyanoferrate(III), the type of conversion(a) was totally excluded,

$$\text{(a)}\ \text{-}\underset{|}{N}\text{-}CH_3 \xrightarrow{[O]} \text{-}\underset{|}{N}\text{-}\overset{OH}{\overset{|}{C}}H_2 \longrightarrow \text{-}\underset{|}{N}\text{-}\overset{O}{\overset{||}{C}}H \quad .$$

Instead, the type of conversion which dominated in the initial step was conversion (b),

$$\text{(b)}\ \text{-}\underset{|}{N}\text{-}CH_2R \xrightarrow{[O]} \text{-}\underset{|}{N}\text{-}\overset{OH}{\overset{|}{C}}HR \longrightarrow \text{-}\underset{|}{N}H + \overset{O}{\overset{||}{H}}CR \quad .$$

In the later stage, the type of conversion was (C),

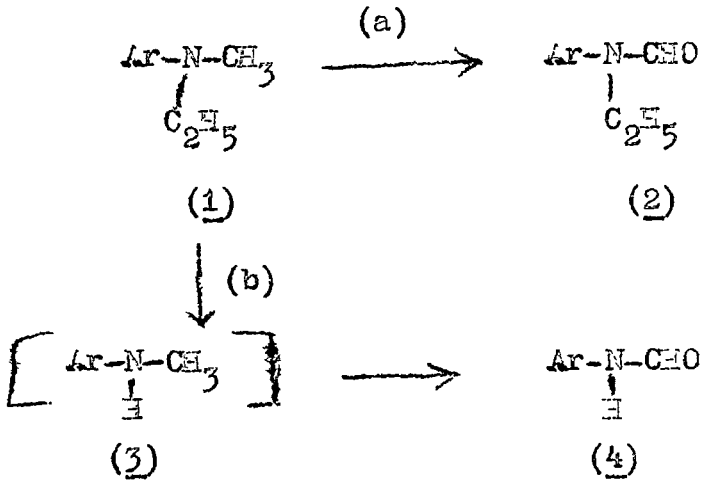
$$\text{(c)}\ \text{-}\underset{|}{N}\text{-}CH_2CH_2R \xrightarrow{[O]} \text{-}\underset{|}{N}\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_2R \xrightarrow{-H_2O}$$

$$\text{-}\underset{|}{N}\text{-}CH = CHR \xrightarrow{[O]} \text{-}\underset{|}{N}\text{-}\overset{OH}{\overset{|}{C}}H\text{-}\overset{OH}{\overset{|}{C}}HR \xrightarrow{[O]}$$

$$\text{-}\underset{|}{N}\text{-}\overset{O}{\overset{||}{C}}H + \overset{O}{\overset{||}{H}}CR$$

In an analogous oxidation of N-ethyl, N-methylaniline (1) by hexacyanoferrate (III) in alkaline medium, it was observed that a mixture of N-ethylformanilide (2)

and formanilide (4) was obtained.



The formation of N-ethylformanilide (2) was an example of a type (a) conversion, while the formation of formanilide(4) represented a type(b) conversion.

Both N-methylaniline and N-ethylaniline were oxidized by alkaline hexacyanoferrate(III) to formanilide. However, the formanilide obtained from the oxidation of N-ethyl, N-methylaniline (1) probably involved the intermediacy of N-methylaniline (3), rather than N-ethylaniline. This transformation involved the cleavage of the C-H bond of the α-carbon of the ethyl group. This would be consistent with the fact that a secondary C-H bond was more reactive than a primary C-H bond.

Oxidation of diphenylamine

The observed second order overall kinetics (first

order in each, substrate and oxidant, Table 4), indicated that the first step involved the direct reaction between the substrate and oxidant. This step was an irreversible one, confirmed by the experimental observation that the addition of hexacyanoferrate (II) ions did not have any effect on the rate of the reaction.

The addition of salts did not have any effect on the rate of the reaction, indicating that the reaction was between an ion and a neutral (dipolar) molecule.

The reaction pathway was via the formation of a radical intermediate (diphenylamino radical, $Ar_2\dot{N}$), which was detected by ESR spectroscopy as a 1:2:1 triplet.

The subsequent step was rapid, resulting in the formation of the product, tetraphenylhydrazine.

The mechanistic pathway can be represented as follows (Scheme 6):

$$Ar_2NH + Fe(CN)_6^{3-} \xrightarrow{\text{slow}} Ar_2\dot{N} + Fe(CN)_6^{4-} + H^+$$

$$Ar_2\dot{N} + Ar_2NH + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} Ar_2N\text{-}NAr_2 + Fe(CN)_6^{4-} + H^+$$

(Scheme 6)

The formation of a radical intermediate in the rate determining step of the reaction was supported by the value of $\rho = -1.0$, which was in the range for reactions proceeding via radical intermediates (115,116).

Oxidation of benzylamine

The rate of the reaction was dependent on the first powers of the concentrations of substrate and oxidant (Table 5), indicating that the first step of the reaction was between the substrate and oxidant.

The lack of any effect on the rate of the reaction by the addition of hexacyanoferrate(II) ions, indicated that the first step of the reaction (electron abstraction step) was an irreversible step.

The addition of salts did not have any effect on the rate of the reaction, suggesting that the reaction was between an ion and a neutral (dipolar) molecule.

The first step of the reaction involved an electron transfer from the nitrogen atom of the amine to the oxidant, resulting in the formation of an aminium radical cation. Examples of stable aminium radical cations have been reported (171-182).

The hydrogen abstraction reaction shown in Scheme 7, leading to the formation of $Ar-\dot{C}H-NH_2$, was a two-step process.

First, the electron was lost (rate-limiting), and then the proton was abstracted by OH^-(fast). This was the function of the required, but kinetically invisible base. This mechanism has been demonstrated for a related system(183).

In neutral or weakly basic solution, it was suggested that the reaction between substituted benzylamines and permanganate proceeds by a mechanism invólving the direct reaction between the amine and permanganate ion in the rate-determining step (94). The predominant process in this oxidation reaction was suggested to be the abstraction of either an α-hydrogen atom or a hydride ion (94), or an electron abstraction from the nitrogen atom (95). In the case of the oxidation of benzylamine by permanganate(94), the pathway suggested was either :

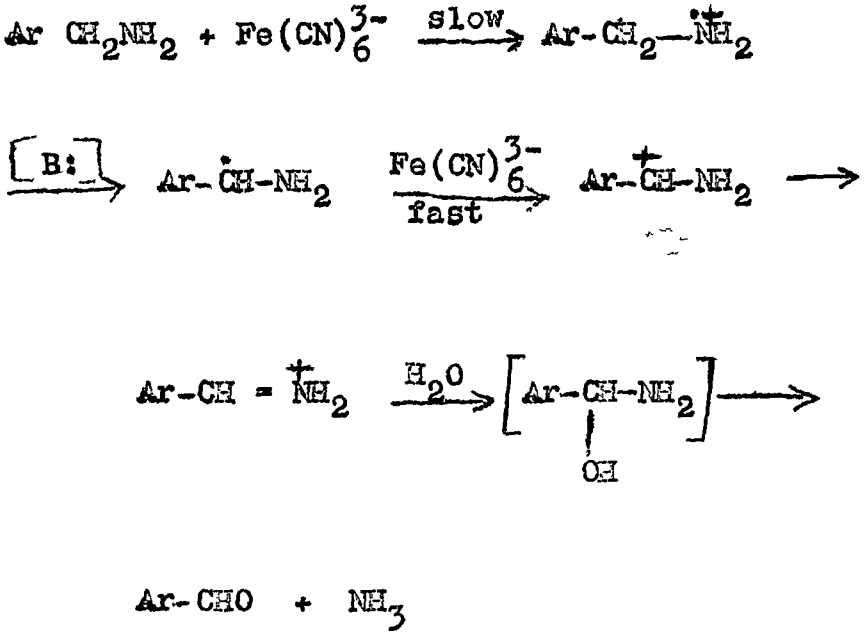
(a) the transfer of a hydrogen atom in the slow step to give Mn(VI) and a radical intermediate, followed by rapid oxidation of the radical, or

(b) the transfer of a hydride ion to give Mn(V) and a cationic intermediate in a single slow step.

In the present investigation, the radical intermediate was characterized by the value of $\rho = -1.0$, by the kinetic isotope effect($k_H / k_D = 6.3$), and by ESR spectroscopy which showed four sets of 1:2:1 triplets.

The radical intermediate thus formed was subject to immediate further oxidation, via the imine conjugate acid, to yield the products, benzaldehyde and ammonia, which were characterized by spectral methods (vide 'Experimental' : Product Analysis).

The sequence of reactions is shown in Scheme 7.



(Scheme 7)

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CHAPTER 3

KINETICS OF OXIDATION OF SOME INORGANIC SULFUR COMPOUNDS

The oxidation of inorganic sulfur compounds has been studied by several workers, using a variety of oxidizing agents.

EARLIER WORK

(a) SULFITE ION

The products formed when sulfite is oxidized are diagnostic of the character of the oxidant. One-electron transfer reagents convert sulfite to dithionate, $S_2O_6^{2-}$ (via the radical anion, $SO_3^{\cdot-}$), whereas two-electron oxidants tend to produce sulfate. Permanganate can produce both products but with an excess of permanganate, or, in basic solution, there was an almost quantitative yield of the sulfate(1). The oxidation of sulfite by oxygen-18 labeled permanganate showed that partial transfer of oxygen (0.2 atoms of oxygen per mole of sulfate formed) from permanganate occurred during the oxidation (2). In acid media, sulfite ion has been oxidized by a variety of transition metal ions, notable among these being $Fe(phen)_3^{3+}$ and Fe^{3+} ions (3-7),

$HCrO_4^-$ ion (8) and $IrCl_6^{2-}$ ion (9). The reaction of sulfite with some quinones had yielded a relationship with the redox potential(10). Various types of metal ion complexes have been employed for the oxidation of sulfite ions, as for example, the Cu(III) tetraglycine complex(11), the Co(III) complex(12), and the tetramine platinum (IV) complex (13). The kinetics of oxidation of sulfite ions by V(V) in acid medium (14), and by N-chloroallylalanine (15) have been reported.

(b) DITHIONITE ION

There was abundant evidence that the dithionite ion, $S_2O_4^{2-}$, underwent rapid fragmentation in aqueous solution. The kinetic schemes were complicated and the product balances were often not complete (16,17). It has been established that the dithionite ion is a strong and versatile two-electron reducing agent (18). The reduction of carbonyl compounds with sodium dithionite has been reported (19,20). Various metal ion complexes have been used to oxidise the dithionite ion (21,22).

(c) THIOSULFATE ION

The oxidation of thiosulfate by alkaline permanganate had yielded the sulfate (23,24). The oxidation of thiosulfate by iodine, forming tetrathionate and iodide, is perhaps the best known reaction of thiosulfate and forms the basis of the titrimetric iodometric quantitative

determinations of oxidizing agents (25,26). The oxidation of thiosulfate by various metal ion oxidants was shown to proceed either through the intermediacy of metal-thiosulfate complexes (27-35) formed prior to electron transfer or without a change in the inner coordination sphere of the metal (36-39). The oxidation of thiosulfate by bromoacetate ion has been reported (40). The oxidation of thiosulfate by tetranitromethane, both in the presence and absence of Cu(II) in aqueous mixtures of methanol and ethanol, has been studied (41). The oxidation of thiosulfate by sodium iodoacetate had reported the formation of ion pairs (42). Octacyanomolybdate (V) has been used for the oxidation of thiosulfate ion (43). The reaction of thiosulfate with methyl iodide in aqueous solutions was reported (44). The oxidation of thiosulfate by W(V) ion has been investigated(45).

(d) THIOCYANATE ION

In the presence of acid permanganate or neutral permanganate, the oxidation of thiocyanate tended to be incomplete (46). With alkaline permanganate, thiocyanate was oxidized to sulfate and cyanate (47). Numerous investigations of the ionic association of ferric ion with thiocyanate ion were reported (48-55). Thiocyanate ion has been oxidized by a variety of oxidizing agents such as Fe^{3+} ions (56-59), hydrogen peroxide (60), the aquocobaltic ion (61),

cytochrome C and porphyrin complexes (62,63), inorganic complexes (64,65), aqueous iodine (66), bismuth (V) ion (67), Cr^{6+} ions (68-70), rhodium (III) complex (71), Vanadium (V) ion (72), $Fe(phen)_3^{3+}$ and its derivatives (73), the $Os(bipy)_3^{3+}$ complex (74), chloramine-T (75,76), Ir (IV) in acid medium(77), acid bromate (78), and by the 12-tungstocobaltate (III) complex (79).

PRESENT WORK

The kinetics of oxidation of inorganic sulfur compounds by hexacyanoferrate (III) in alkaline medium, has not received adequate attention. The present work is a detailed kinetic investigation of the oxidation of some inorganic sulfur compounds (sulfite, metabisulfite, dithionite, thiosulfate and thiocyanate ions) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere.

Stoichiometry (vide 'Experimental'):

The stoichiometry of the reactions were determined to be:

(a) For Sulfite

$$2\ SO_3^{2-} + 2Fe(CN)_6^{3-} \longrightarrow S_2O_6^{2-} + 2Fe(CN)_6^{4-}\ .$$

(b) For metabisulfite

$$S_2O_5^{2-} + 2Fe(CN)_6^{3-} + 2\ OH^- \longrightarrow S_2O_6^{2-} + 2\ Fe(CN)_6^{4-} + H_2O.$$

(c) For dithionite

$$S_2O_4^{2-} + 2Fe\ (CN)_6^{3-} + 4\ OH^- \longrightarrow\ 2SO_3^{2-} + 2Fe(CN)_6^{4-} + 2H_2O$$

(d) For thiosulfate

$$2\ S_2O_3^{2-} + 2Fe(CN)_6^{3-} \longrightarrow\ S_4O_6^{2-} + 2\ Fe(CN)_6^{4-}.$$

(e) For thiocyanate

$$2\ SCN^- + 2Fe(CN)_6^{3-} \longrightarrow (SCN)_2 + 2Fe(CN)_6^{4-}.$$

$$3(SCN)_2 + 4\ H_2O \longrightarrow CN^- + SO_4^{2-} + 5\ SCN^- + 8H^+$$

Effect of substrate and oxidant

The rates of the reactions were observed to be dependent on the first powers of the concentrations of each, substrate and oxidant (Tables 1 - 5).

Table 1: Effect of substrate and oxidant

/ Sulfite / (10^3 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^4 x k_{obs} (s^{-1})
7.5	1.0	6.2
10.0	1.0	8.3
25.0	1.0	20.8
50.0	1.0	42.0
75.0	1.0	63.0
10.0	0.75	8.4
10.0	0.50	8.2
10.0	0.10	8.3

/ NaOH / = 0.1 M; μ = 0.05 M; temp. = 35°C.

Table 2: Effect of substrate and oxidant

/ $K_2S_2O_5$ / (10^3 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^4 x k_{obs} (s^{-1})
7.5	1.0	10.8
10.0	1.0	14.5
25.0	1.0	36.0
50.0	1.0	73.0
7.5	0.75	10.5
7.5	0.50	11.0
7.5	0.10	10.8

/ NaOH / = 0.1 M; μ = 0.05 M; temp. = 35°C.

Table 3: Effect of substrate and oxidant

/ Dithionite / (10^2 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^4 x k_{obs} (s^{-1})
1.0	1.0	2.2
2.5	1.0	5.6
5.0	1.0	11.0
10.0	1.0	22.0
25.0	1.0	56.0
1.0	0.75	2.0
1.0	0.50	2.2
1.0	0.10	2.0

/ NaOH / = 0.1 M; μ = 0.05 M; temp. = 35°C.

Table 4 : Effect of substrate and oxidant

/ Thiosulfate / (M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	$10^5 \times k_{obs}$ (s^{-1})
0.1	1.0	2.1
0.25	1.0	5.2
0.50	1.0	10.6
1.0	1.0	21.4
0.5	0.75	10.7
0.5	0.5	10.5
0.5	0.1	10.7

/ NaOH / = 0.1 M; μ = 0.05 M; temp. = 35°C.

Table 5 : Effect of substrate and oxidant

/ Thiocyanate / (M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	$10^5 \times k_{obs}$ (s^{-1})
0.1	1.0	0.7
0.5	1.0	3.5
1.0	1.0	7.0
1.5	1.0	10.8
2.0	1.0	14.2
2.0	0.5	14.0
2.0	2.5	14.2
2.0	5.0	14.0
2.0	10.0	14.0

/ NaOH / = 0.5 M; μ = 0.05 M; temp. = 50°C.

Plots of k_{obs}, the pseudo first order rate constant, against a ten-fold range of concentration of substrate, gave straight lines passing through the origin, indicating that the rate of oxidation was dependent on the first power of the concentrations of the substrate. This was further seen by the constant values of k_2, the second order rate constant. When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant (ten-fold range) indicating a first order dependence of the rate of the reaction on the concentration of the oxidant (Tables 1-5).

Effect of alkali

The rates of the reactions were dependent on the first powers of the concentrations of alkali in the range studied in the case of the sulfite, bisulfite and dithionite ions (Table 6). In the case of the thiosulfate and thiocyanate ions, the rates were independent of the concentrations of alkali in the range studied.(Table 7).

Table 6. Effect of NaOH

Substrates (0.01 M)	$10^4 \times k_{obs}$, s^{-1}, at 35°C for / NaOH / 0.025 M	0.050 M	0.10 M	0.25 M	at 0.50 M
Sulfite	2.1	4.2	8.5	21.2	42.0
Bisulfite*	2.7	5.4	10.8	27.5	55.0
Dithionite	0.5	1.0	2.2	5.5	11.0

$K_3Fe(CN)_6$ = 1 x 10^{-3} M; μ = 0.05 M

*/ Substrate / = 7.5 x 10^{-3} M

Table 7 : Effect of NaOH

Substrates (0.5 M)	$10^5 \times k_{obs}$, s^{-1}, at 35°C for / NaOH / 0.025 M	0.05 M	0.10 M	0.25 M	at 0.50 M
Thiosulfate	10.4	10.5	10.6	10.3	10.5
*Thiocyanate	14.0	14.5	14.2	14.0	14.2

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; μ = 0.05 M

* / Thiocyanate / = 2.0 M; temp. = 50°C.

Rate law

Under the present experimental conditions, the rate law could be expressed as:

(a) For Sulfite, bisulfite and dithionite ions

$$\text{Rate} = -\frac{d/Fe(CN)_6^{3-}/}{dt} = k_{obs} / \text{Substrate}/ / Fe(CN)_6^{3-} / / OH^- / \quad \ldots\ldots\ldots \quad (1).$$

(b) For thiosulfate and thiocyanate ions

$$\text{Rate} = -\frac{d/Fe(CN)_6^{3-}/}{dt} = k_{obs} / \text{Substrate}/ / Fe(CN)_6^{3-} / \quad \ldots\ldots\ldots \quad (2).$$

The pseudo first order rate constant, k_{obs}, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation (80):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \quad \ldots\ldots\ldots \quad (3)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time, t (vide 'Experimental' : Calculations).

Effect of temperature

The rates of the reactions were influenced by changes in temperature (Table 8). Plots of log k_{obs} against

the reciprocal of temperature were linear (Figs. 1 - 5), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies of the reactions (vide 'Experiemntal' : Calculations). The other activation parameters have been evaluated and are shown in Table 9.

Table 8 : Effect of temperature

Substrates	$10^4 \times k_{obs}$, s^{-1}, at temperatures ($\pm$ 0.1°C)				
	30.0	35.0	40.0	45.0	50.0
Sulfite	6.1	8.3	11.0	14.8	20.3
Bisulfite	7.9	10.8	16.0	19.6	—
Dithionite	1.4	2.2	4.5	7.0	10.2
Thiosulfate	0.6	1.1	2.2	4.4	9.0
*Thiocyanate	14.2[a]	17.0[b]	20.0[c]	23.0[d]	26.5[e]

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; / NaOH / = 0.1 M;

μ = 0.05 M.

/ Sulfite / = / Dithionite / = 0.01 M; / Bisulfite / = 7.5x10^{-3}M;

/ Thiosulfate / = 0.1 M.

* / Thiocyanate / = 2.0 M; / NaOH / = 0.5 M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3} M; μ = 0.05 M; [a]50°C, [b]55°C; [c]60°C, [d]65°C, [e]70°C.

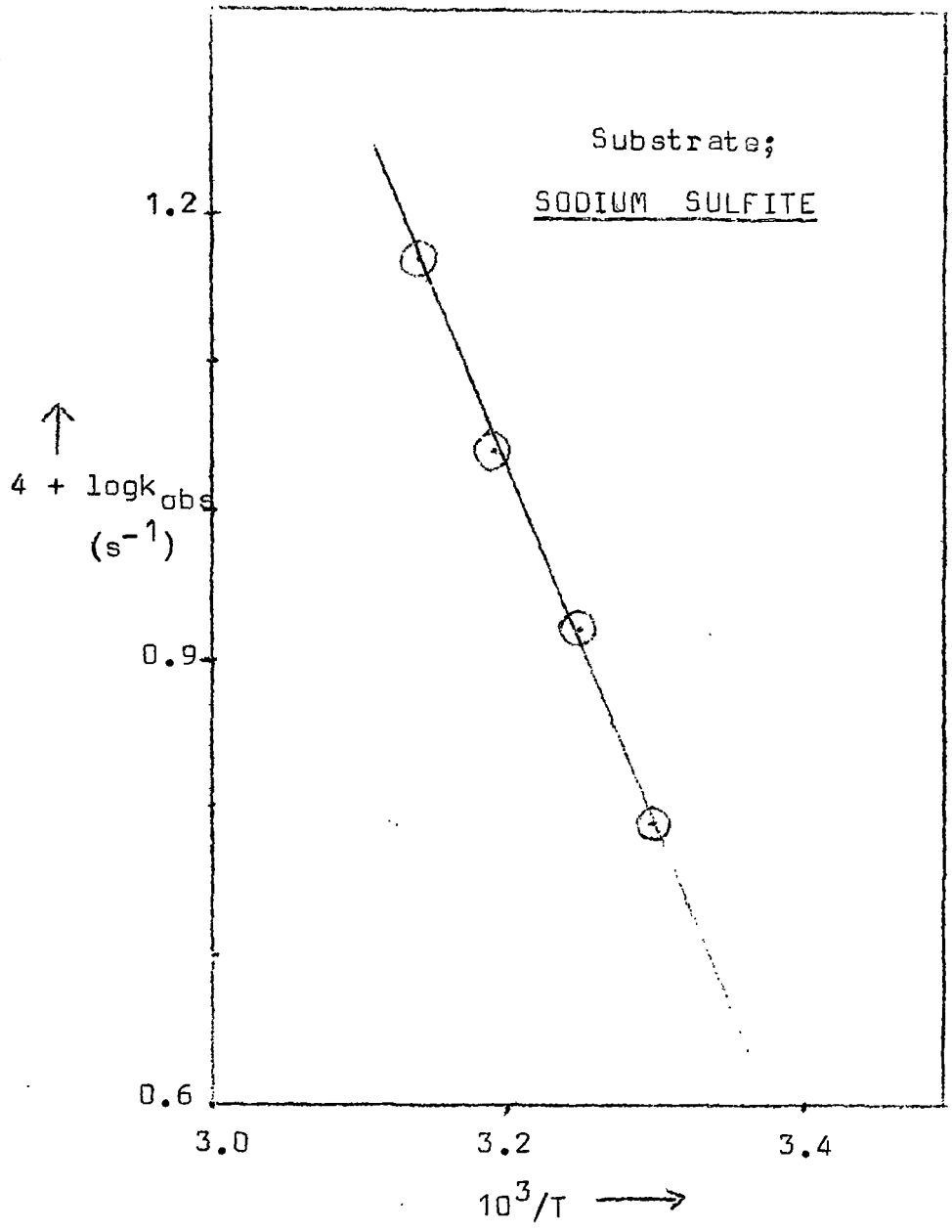

Fig. 1 . Plot of log k_{obs} against the reciprocal of temperature (Substrate:; SODIUM SULFITE)

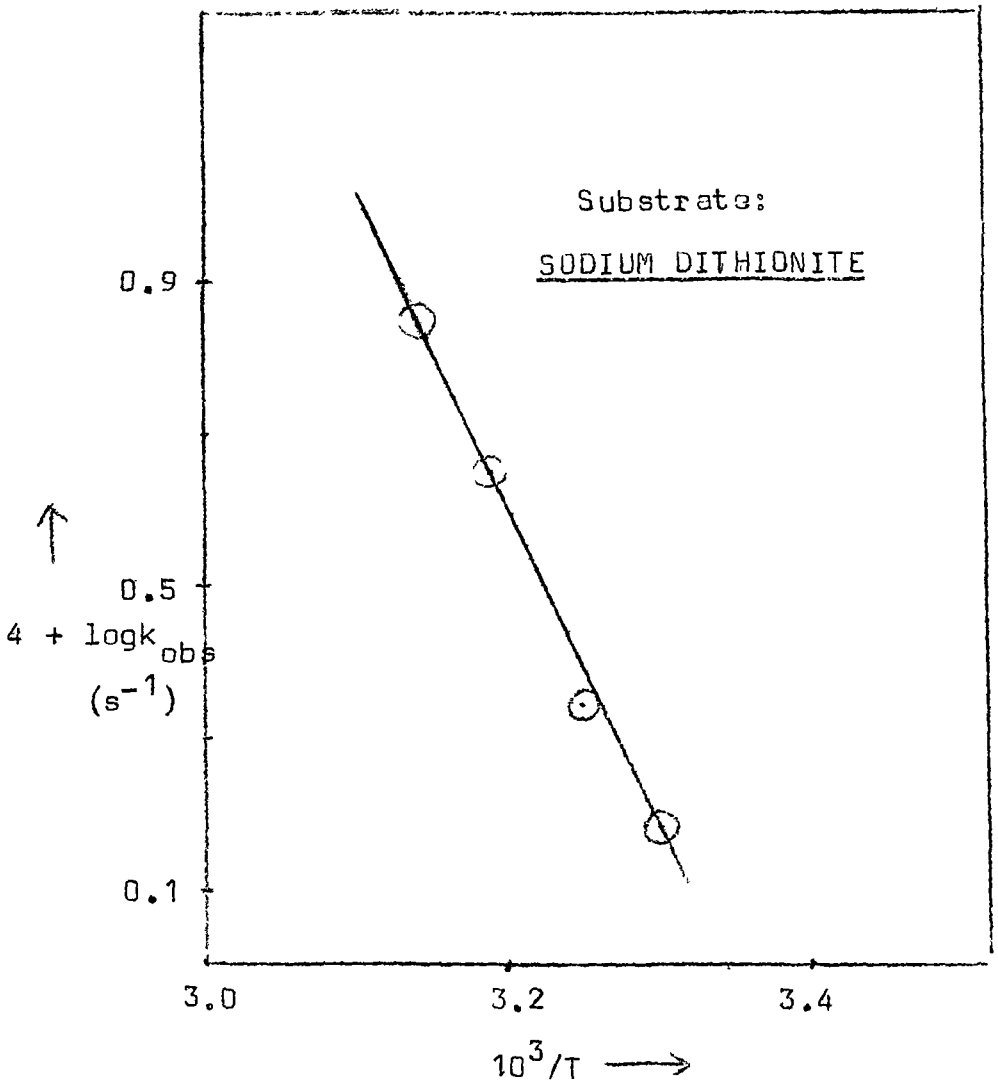

Fig. 2 . Plot of log k_{obs} against the reciprocal of temperature (Substrate : SODIUM DITHIONITE)

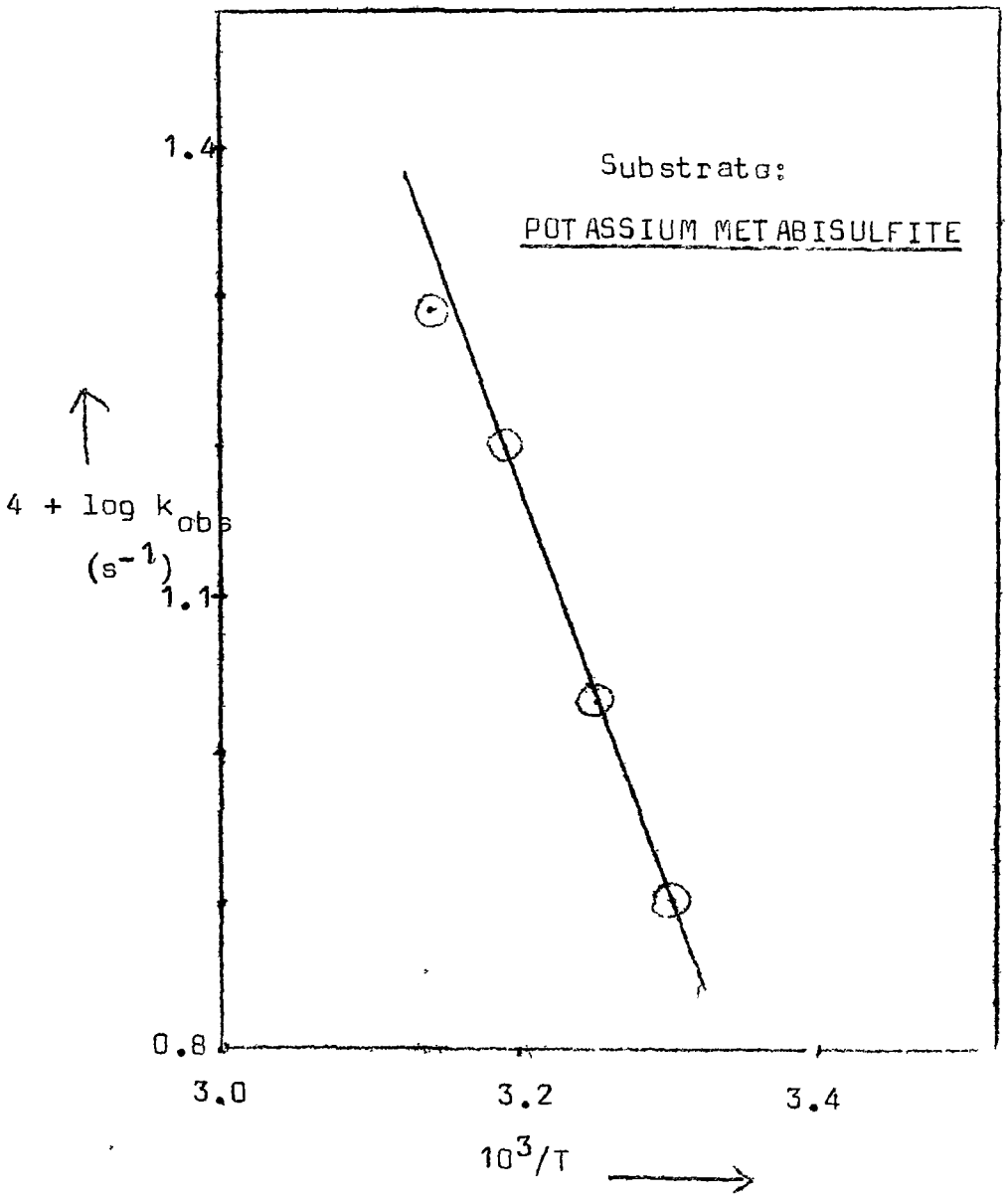

Fig. 3 . Plot of log k_{obs} against the reciprocal of temperature (Substrate: POTASSIUM METABISULFITE)

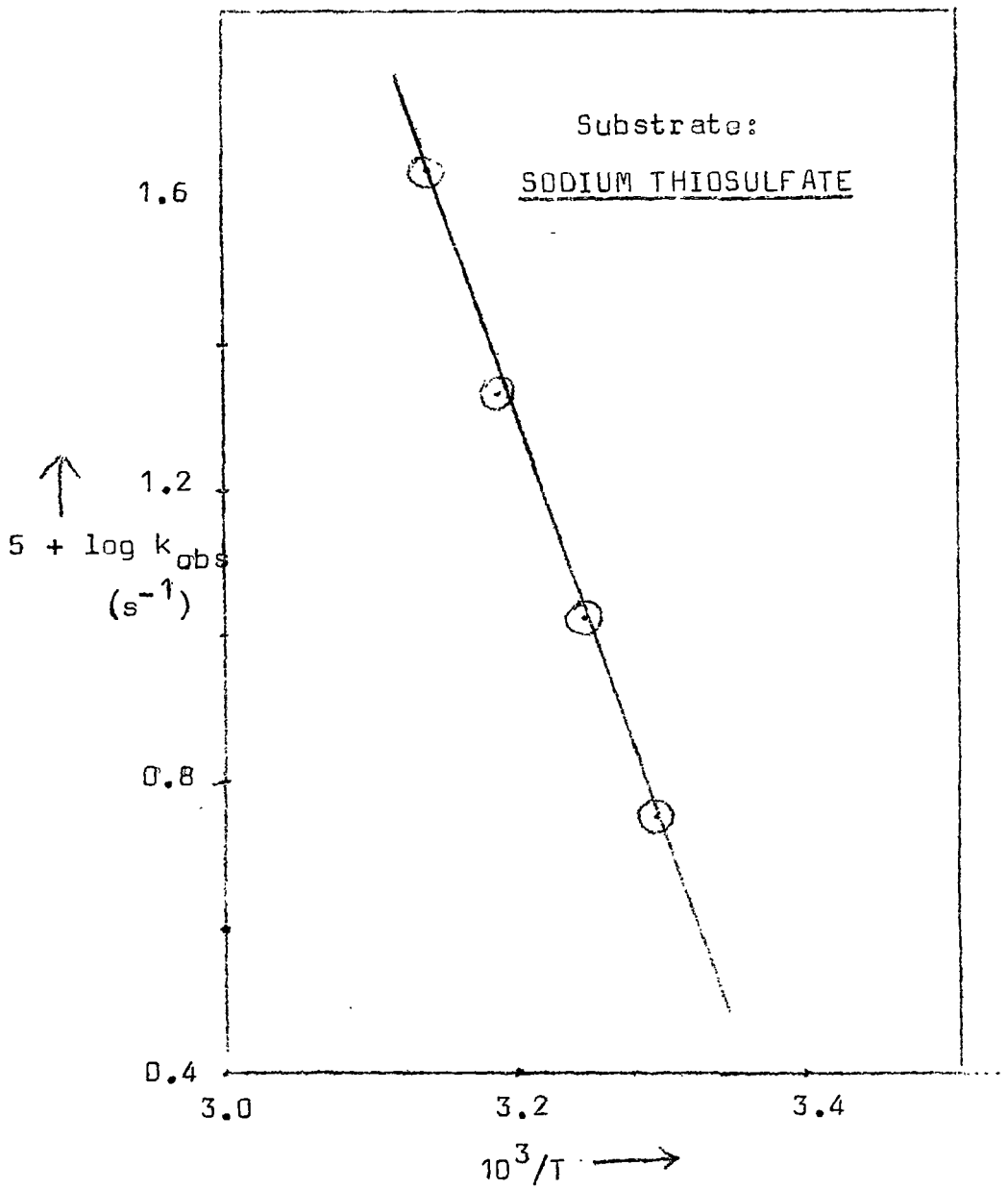

Fig. 4 . Plot of log k_{obs} against the reciprocal of temperature (Substrate : SODIUM THIOSULFATE)

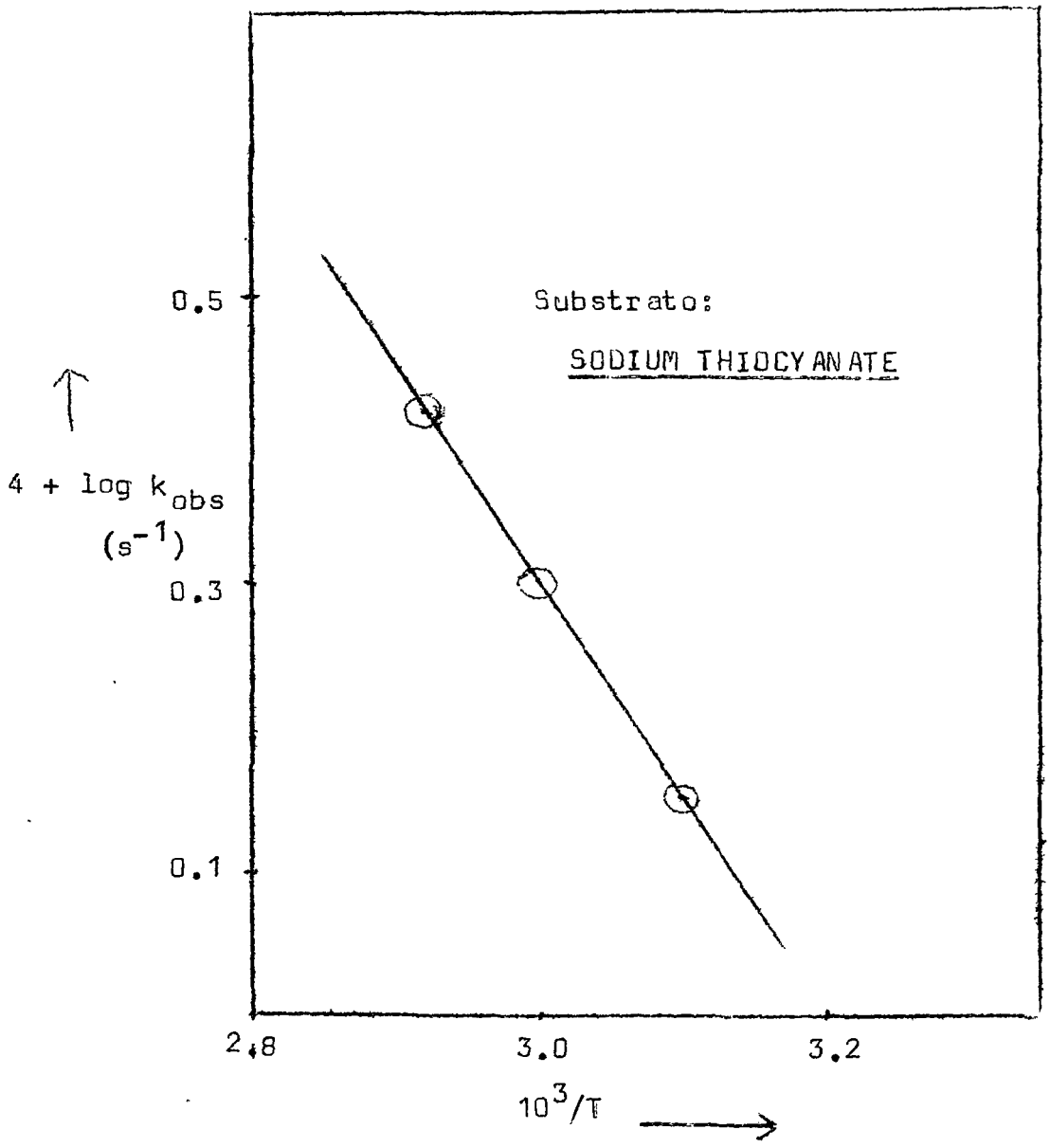

Fig. 5. Plot of log k_{obs} against the reciprocal of temperature (Substrate : SODIUM THIOCYANATE)

Table 9 : Activation Parameters

Substrates	E (kJ mol^{-1})	A (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
Sulfite	47±2	7.5×10^{4}	44±2	-160±5
Bisulfite	46±2	7.0×10^{4}	43±2	-160±5
Dithionite	90±5	4.7×10^{11}	87±5	- 30±2
Thiosulfate	107±4	1.7×10^{14}	104±4	- 19±2
Thiocyanate	28±2	6.3×10^{4}	25±2	-180±5

Effect of ionic strength

The variation of ionic strength by using KCl (μ = 0.05 M to 0.50 M), did not have any effect on the rates of the reactions.

Effect of added $K_4Fe(CN)_6$

The addition of $K_4Fe(CN)_6$ in the concentration range, 1.0×10^{-4} M to 1.0×10^{-3} M, did not have any influence on the rates of the reactions.

Radical intermediates

(a) From the oxidation of sulfite ion

The kinetics were performed in a 10 ml mixture of 2-propanol: water (1:1). After completion of a kinetic run,

as evidenced by the disappearance of the yellow colour due to $Fe(CN)_6^{3-}$, 2ml of 50% aqueous NaOH and 2 ml of 10% 4-hydroxy-3-methoxybenzaldehyde in methanol were added. The resulting solution was diluted with water (approximately 5 ml), and heated to 60°C in a water bath. A yellow colouration was obtained, indicating that 2-propanol had been oxidized to propanone. Solutions containing no reactants and only SO_3^{2-} were used as blanks. The reaction between 2-propanol and hexacyanoferrate(III) did not proceed. This evidence strongly suggested that a radical mechanism was important in the reaction of sulfite ions and hexacyanoferrate(III).

The free radical was not observed using ESR (E-4, Varian). It was possible that the radical was present in very low concentrations, and hence could not be detected, under the present experimental conditions.

The presence of a radical species ($SO_3^{\cdot-}$) in reactions involving the oxidation of sulfite ions, and the inhibitive action of alcohols on such oxidation reactions, has been suggested in an earlier investigation (81).

(b) From the oxidation of dithionite ion

The structure of sodium dithionite (82) was marked by an unusually long sulfur-sulfur bond, suggesting that SO_2^- radicals might readily be formed from dithionite. The oxidation reaction of dithionite may well be explained by

assuming that the rather unstable ion splits according to the equation

$$S_2O_4^{2-} \rightleftharpoons 2\ SO_2^{\cdot-}$$

to form two radical ions. These may then undergo further oxidation. A free radical in low concentrations in moist dithionite (83,84), and in deaerated aqueous solutions (85) was detected. Upon the basis of the work done by several investigators (82,83,86), it was reasonable to expect that the dithionite anion ($S_2O_4^{2-}$) in aqueous solution was in equilibrium with paramagnetic $SO_2^{\cdot-}$ radical ions. The presence of the $SO_2^{\cdot-}$ radical ion has been confirmed by ESR spectroscopy (87,88). In the present investigation, ESR spectroscopy gave a single broad line with a hyperfine splitting constant of 14.0 gauss, and a value of $g_{av} = 2.0060 \pm 0.0004$. Thus, the dithionite ion dissociates reversibly in aqueous solution, $S_2O_4^{2-} \rightleftharpoons 2\ SO_2^{\cdot-}$, which is supported by the value of the isotropic hyperfine coupling constant (14.0 gauss), showing that the electron is in a π-orbital associated with only one sulfur atom.

The reduction reactions of biochemical species by dithionite ions had shown that the dominant reductant was the $SO_2^{\cdot-}$ radical (89-96).

(c) From the oxidation of thiocyanate ion

The existence of the ion-radical $(SCN)_2^{\bullet-}$, as an intermediate in the reactions of thiocyanate ions has been established (56,73,74,77,97). Simple electron transfer from SCN^- to the oxidant to give a $SCN^\bullet$ radical was not favoured thermodynamically (98,99). An earlier investigation (73) had established that electron transfer from SCN^- to Fe(III) $phen_3$ to give a $SCN^\bullet$ radical was thermodynamically unfavourable, since the radical, $SCN^\bullet$, was a very high-energy species. Unfavourable energy requirements were suggested to account for the complicated mechanism in the oxidation of I^- and CN^- ions by $Fe(H_2O)_6^{3+}$ (refs. 100,101) and $Fe(CN)_6^{3-}$ (ref. 102). Instead, radical ions such as $I_2^{\bullet-}$ and $(CN)_2^{\bullet-}$ were thought to be involved (103).

Mechanism

(a) Oxidation of sulfite ion

The redox potentials (98) for the couples SO_3^{2-} / $S_2O_6^{2-}$ and $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ were thermodynamically favourable for electron transfer between the substrate and oxidant. Oxidation reactions by hexacyanoferrate (III) mostly involve outer-sphere electron change, and the formation of radical intermediates has been well - documented (104 - 106).

In the present investigation, the reaction between the sulfite ion and hexacyanoferrate (III) was observed to depend on the first powers of the concentrations of substrate, oxidant and alkali (Tables 1,6). Evidence has been presented to suggest that a radical intermediate was formed in the slow step of the reaction. This radical intermediate was characterized (vide 'Radical intermediates'). The presence of SO_3^- radical in reactions involving the oxidation of SO_3^{2-} ion, and the inhibitive action of alcohols on such reactions has been suggested (81).

There was no spectral evidence for the presence of any complex formation between sulfite ion and hexacyanoferrate (III). Repeated and continuous scanning of the reaction solutions (from 250 nm to 650 nm), even with higher initial concentrations of the reactants, did not show any peak or shoulder other than those corresponding to the reactants and the products. When the experiment was conducted in the presence of $^{14}CN^-$, there was no labelled cyano-ligand in the $Fe(CN)_6^{4-}$ product, ensuring the absence of cyano exchange. Thus, the formation of an intermediate complex between the sulfite ion and hexacyanoferrate (III), in the present investigation, seems highly unlikely. Furthermore, the formation of an intermediate complex between the substrate and oxidant would be facilitated by the presence of a sulfite

ligand of very low Lewis basicity (107), which would be able to substitute, or attach itself to, a cyano-ligand in a non-labile low-spin d^5-octahedral complex, $Fe(CN)_6^{3-}$. In all probability, this would inherently be forbidden. Finally, the experimental observation that the rate of the reaction was first order in substrate and oxidant rules out the possibility of the reaction proceeding through an intermediate complex formation. The rate of the reaction was unaffected by variations in the ionic strength of the medium and by changes in the concentration of added $K_4Fe(CN)_6$. The absence of complex formation rules out the possibility of an inner sphere pathway, as suggested earlier (108).

The first order dependence of the rate of the reaction on the concentrations of both, substrate and oxidant, suggested that the mechanism of the oxidation process was via an outer sphere process. This involved the direct reaction of sulfite ion and hexacyanoferrate (III) to give a radical species, which underwent rapid dimerization to yield dithionate as the product. This product was isolated and characterized (vide 'Experimental': Product analysis).

The mechanistic pathway can be represented as follows:

$$SO_3^{2-} + Fe(CN)_6^{3-} \xrightarrow{\text{slow}} SO_3^{\cdot -} + Fe(CN)_6^{4-}$$

$$2\ SO_3^{\cdot -} \longrightarrow S_2O_6^{2-}$$

(b) Oxidation of Thiosulfate

The redox potentials (98) for the couples $S_2O_3^{2-}$ / $S_4O_6^{2-}$ and $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ were thermodynamically favourable for electron transfer between thiosulfate and hexacyanoferrate (III). Hence, the reaction between $S_2O_3^{2-}$ ion and $Fe(CN)_6^{3-}$ should proceed by a direct interaction between the reactants.

Complexes of Cu (II), Co (III), Au (III), Cr (IV) and Fe (III) have been used for the oxidation of thiosulfate ion (27-35). Kinetics and other evidences suggested that in all these oxidation reactions, precursor metal-thiosulfato complexes (where the metal has lost one formal oxidation state, and thiosulfate has gained one) were formed in an equilibrium step preceding the electron transfer.

However, all attempts at characterizing any intermediate complex between the thiosulfate ion and hexacyanoferrate (III) by repeated and continuous scanning of the reaction mixtures (from 250 nm to 650 nm), even with higher initial concentrations of the reactants, were unsuccessful. There was no peak or shoulder other than those corresponding to the reactants and the products. When the experiment was carried out in the presence of $^{14}CN^-$, there was no labelled cyano-ligand in the $Fe(CN)_6^{4-}$ product, establishing the absence of any cyano exchange. Hence, the formation of an intermediate

involving the thiosulfate ion and hexacyanoferrate (III), in the present system, seemed highly unlikely. Moreover, any direct interaction between the thiosulfate ion and hexacyanoferrate (III) to form an intermediate complex necessitates a thiosulfato-ligand of very low Lewis basicity (107) to substitute, or attach itself to, a cyano-ligand in a non-labile low-spin octahedral complex, $Fe(CN)_6^{3-}$. In all probability, this would inherently be forbidden.

In the present investigation, the reaction between the thiosulfate ion and hexacyanoferrate (III) was observed to be dependent on the first powers of the concentrations of the substrate and oxidant (Table 4). The rate of the reaction was insensitive to variations in the ionic strength and to added $Fe(CN)_6^{4-}$ ions. These experimental observations rule out the possibility of the reaction proceeding through an intermediate complex formation.

The addition of radical inhibitors such as mannitol and acrylonitrile, had no effect on the observed rate of the reaction, suggesting that the involvement of free radicals in the rate determining step of the reaction was unlikely.

Since $Fe(CN)_6^{3-}$ required one electron to be reduced to $Fe(CN)_6^{4-}$, the reaction between the thiosulfate ion and hexacyanoferrate (III) would occur by a one-equivalent

electron transfer, giving rise to a singly charged anion ($S_2O_3^-$), thus :

$$S_2O_3^{2-} + Fe(CN)_6^{3-} \xrightarrow{slow} S_2O_3^- + Fe(CN)_6^{4-} \quad \ldots\ldots \quad (1)$$

This one-electron change involving $Fe(CN)_6^{3-}$ and thiosulfate (Eq.1) could take place only with a high activation enthalpy, because an unstable $S_2O_3^-$ species was formed. The $\Delta H^{\neq}$ value obtained was 104 ± 4 kJ mol^{-1} (Table 9).

The solvent isotope effect was measured by preparing identically buffered reaction mixtures in water and in 95% D_2O. The ratio of k_{H_2O} / k_{D_2O} observed was 1.45. An estimation of the solvent isotope effect on the reaction between the thiosulfate ion and hexacyanoferrate (III) was made earlier(39). If the reactants were $S_2O_3^{2-}$ and $S_2O_3^-$, then on the basis of a knowledge of the ΔpK values for the relevant acids in going from H_2O to D_2O, the relevant activities of the various ions in these solvents (H_2O and D_2O) could be calculated. Theoretically, this predicted a value of k_{H_2O} / k_{D_2O} = 1.50. This would support the formation of the $S_2O_3^-$ species in the rate determining step of the reaction (Eq. 1).

In the present investigation, the direct reaction between the thiosulfate ion and hexacyanoferrate (III) gave rise to $S_2O_3^-$ and $Fe(CN)_6^{4-}$ ions. The rapid dimerization of $S_2O_3^-$ would yield the product, tetrathionate ions ($S_4O_6^{2-}$).

Indeed, the rapid dimerization of $S_2O_3^-$ to yield $S_4O_6^{2-}$ was postulated in several oxidation reactions involving the thiosulfate ions (30,31).

The product, tetrathionate ($S_4O_6^{2-}$) ions, was isolated and characterized (vide 'Experimental' : Product analysis).

The mechanism of oxidation of thiosulfate ions by hexacyanoferrate (III) can be represented as follows:

$$S_2O_3^{2-} + Fe(CN)_6^{3-} \xrightarrow{\text{slow}} S_2O_3^- + Fe(CN)_6^{4-}$$

$$2\ S_2O_3^- \longrightarrow S_4O_6^{2-}$$

(c) Oxidation of Dithionite

The structure of the dithionite ion was confirmed by crystallographic studies (82). The S-S bond in dithionite (2.389 Å) was much longer than the S-S bonds in disulfides or polysulfides (2.0 Å to 2.15 Å). This long bond in dithionite (2.389 Å) together with the unusual shape of the molecule with eclipsed SO_2 groups, was due to each sulfur atom forming two pd hybrid orbitals, one of which was used to bond to the other atom. The weak bonding was consistent with the strong reducing properties and with the rapid exchange between $S_2O_4^{2-}$ and labeled $^*SO_2$. The long sulfur-sulfur bond would enable the facile formation of SO_2^- radicals,

$$S_2O_4^{2-} \rightleftharpoons 2\ SO_2^{\cdot-}\ ,$$

which would then undergo further oxidation.

In the present investigation, the rate of the reaction was first order in both, $Fe(CN)_6^{3-}$ and $S_2O_4^{2-}$ (Table 3). This would suggest that the formulated fission

$$S_2O_4^{2-} \rightleftharpoons 2\ SO_2^{\cdot-} \qquad (1)$$

does really occur. The presence of the $SO_2^{\cdot-}$ radical was shown by ESR spectroscopy as a single broad line with a hyperfine splitting constant of 14.0 gauss, and a value of $g_{av} = 2.0060 \pm 0.0004$ (vide 'Radical intermediates'). The $SO_2^{\cdot-}$ radical was shown to be a stronger reducing agent than $S_2O_4^{2-}$ (109), and was convincingly implicated as the reductant of various biological materials (89-96).

It has been shown (vide 'Stoichiometry') that each mole of $S_2O_4^{2-}$ consumed two moles of $Fe(CN)_6^{3-}$. The redox potentials (98) for the couples $S_2O_4^{2-}$ / SO_3^{2-} and $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ were thermodynamically favourable for electron transfer between dithionite and hexacyanoferrate(III), in the overall reaction process.

The product, sulfite (SO_3^{2-}) ion, was characterized (vide 'Product analysis').

The mechanism of oxidation of dithionite ion by

hexacyanoferrate (III) can be represented as follows:

$$S_2O_4^{2-} \rightleftharpoons 2\ SO_2^{\cdot-}$$

$$2\ SO_2^{\cdot-} + 2Fe(CN)_6^{3-} + 4\ OH^- \longrightarrow 2\ SO_3^{2-} + 2Fe(CN)_6^{4-} + H_2O\ .$$

(d) Oxidation of Thiocyanate

In the present investigation, the rate of the reaction was observed to be dependent on the first powers of the concentrations of the substrate and oxidant (Table 5). Variations in the ionic strength of the medium, as also changes in the concentration of added $Fe(CN)_6^{4-}$ ions, did not have any effect on the rate of the reaction. These data would suggest an outer sphere electron transfer process.

The presence of the ion radical, $(SCN)_2^{\cdot-}$, was observed, in accordance with earlier reports wherein the formation of the ion radical, $(SCN)_2^{\cdot-}$, had been established (56,73,74,77,97).

The mechanism of the reaction can be represented as:

$$Fe(CN)_6^{3-} + 2\ SCN^- \longrightarrow Fe(CN)_6^{4-} + (SCN)_2^{\cdot-}$$

$$Fe(CN)_6^{3-} + (SCN)_2^{\cdot-} \longrightarrow Fe(CN)_6^{4-} + (SCN)_2$$

Thiocyanogen, $(SCN)_2$, can decompose in aqueous medium, thus:

$$3(SCN)_2 + 4\ H_2O \longrightarrow CN^- + SO_4^{2-} + 5\ SCN^- + 8H^+.$$

The oxidation of thiocyanate ion by hexacyanoferrate (III) produced thiocyanogen, $(SCN)_2$. The redox potentials (98) for the couples, 2 SCN^- / $(SCN)_2$ and $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$, were thermodynamically favourable for electron transfer between thiocyanate and hexacyanoferrate(III). An earlier investigation had established that thiocyanogen was the product of thiocyanate oxidation (58).

In the present investigation, the products formed were the sulfate ions and the cyanide ions, which have been characterized (vide 'Experimental' : Product analysis). It was not surprising that SO_4^{2-} and CN^- were the oxidation products, since thiocyanogen, $(SCN)_2$, was known to decompose readily in aqueous medium (110).

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CHAPTER 4

KINETICS OF OXIDATION OF SOME ORGANIC SULFUR COMPOUNDS.

Aliphatic and aromatic thiols have been oxidized by a variety of reagents to disulfides and to higher oxidation products, depending on the specific reaction conditions.

EARLIER WORK

Aliphatic and aromatic thiols were converted to disulfides in aqueous or alcoholic peroxide solutions in both, acidic and alkaline media (1,2). Higher molecular weight thiols, in the form of their copper salts, were oxidized by peroxides (3). In the presence of aliphatic amines, peroxides were used for the oxidation of thiols in hydrocarbon solvents(4). The oxidation of thiols by hydrogen peroxide, alkyl hydroperoxides and peroxy acids gave the disulfide (5). Nickel peroxide has been found to be an efficient reagent for the oxidation of thiols (6).

Considerable attention has been focused on systems of biological interest, and electrochemical techniques have been used for the quantitative analysis of thiol and disulfide groups in organic compounds (7-16). The electrochemical

oxidation of cysteine, as well as other thiols, occurred by a one-electron process giving cystine, which on further oxidation gave cysteic acid (17-20).

The oxidation of thiols by halogens yielded products which were dependent upon the halogen and the reaction medium. In aqueous solvents, chlorine and bromine reacted with thiols to give sulfonyl halides or sulfonic acids (21-23). Under anhydrous conditions, chlorine and bromine react with thiols to give disulfides (24).

Sulfenyl halides were susceptible to nucleophilic attack (21, 23, 25), as for example :

$$RSX + NuH \longrightarrow RS\,Nu + HX \qquad (1)$$

($NuH = R_2NH$, HSCN, ROH, RSH).

Excess thiol reacted with these sulfenyl halides to give the disulfide, thus:

$$RSX + RSH \longrightarrow RSSR + HX \qquad (2).$$

Chloramine - T has been used for the oxidation of thiols (26).

Thiols have been oxidized by dimethyl sulfoxide to the corresponding disulfides in high yields (27-30). A correlation was suggested between the pK_a and the activation energy(29). When an optically active thiol was oxidized by an excess of sulfoxide, optically active sulfoxides were recovered (31).

Thiosulfonium ions have been suggested as intermediates in the oxidation of thiols by dimethyl sulfoxide (32).

The reaction of thiols with diethyl azodicarboxylate gave the disulfides (33). These reactions were catalyzed by triphenylphosphine, and involved the intermediate formation of radicals or radical ions (34).

Radical anion intermediates were detected, by esr spectroscopy, in the oxidation of thiols to disulfides by nitrobenzene and nitrosobenzene (35,36). The oxidation of thiols by iodosobenzene in refluxing dioxan, gave the disulfides in good yields (37).

Metal ions such as Ce^{4+}, Co^{3+}, V^{5+} and Cr^{6+} ions in acid solution have been used for the oxidation of thiols to disulfides (38-40). The presence of thiyl radicals has been confirmed in the oxidation of several thiols (41). The oxidation of thioglycolic acid, cysteine and glutathione by Mo^{5+} and Mo^{6+} ions, showed the importance of the nature and stability of the complexes between metal ions and thiols (42). Mn^{7+} ions has been used for the oxidation of pyrimidine thiols (43). Lead tetraacetate has been used to convert thiols to disulfides (44-47).

The oxidation of thiols to disulfides by manganic acetylacetonate did not reveal the presence of thiyl radicals (48). Cupric complexes in non-polar media (49), iron cluster complexes (50), and Co(II) complexes (51) have been used for the oxidation of thiols to disulfides.

Metal oxides (CrO_3, MnO_2, Fe_2O_3, Co_2O_3, CuO, PbO_2) have been used to oxidize thiols to disulfides, at low temperatures in xylene or chloroform solution (47,52,53). When these reactions were performed in the presence of an alkene, the formation of large amounts of thiol addition products suggested the intermediate formation of thiyl radicals (47,52,53).

Thiols undergo facile oxidation when exposed to air. The oxidation of thiols catalyzed by strong bases (54) and the effect of solvent (55-57) on these oxidations has been reported. The amine-catalyzed oxidation of thiols has been investigated (58-59). The effect of the addition of heavy metal ions to basic aqueous solutions of thiols (60-64), as also the effect of ligands on the rates of oxidation of thiols have been studied (64,65). It was suggested that the metal-catalyzed oxidation of thiols in alkaline media was based on an electron-transfer from the metal in its higher oxidation state, to the thiol, via an inner sphere process. Outer sphere processes were suggested when strong complexing agents prevented the entry of the thiol into the coordination sphere of the metal (66). For example, in the case of cyanide complexes, it was assumed that the oxidation of thiols occurred by an outer sphere process, involving the intermediacy of thiyl radicals (66).

In the absence of oxygen, flavine derivatives have been used to convert thiols to disulfides(67,68).

In basic media, hydroquinone (69) and p-phenylene-diamine derivatives (70,71) have been used to catalyze the autooxidation of thiols to disulfides. The auto-oxidation of thiols to disulfides has been reported (72).

The rate of cooxidation of thiols (when an alkene or an acetylene was oxidized together with the thiol) was dependent on both, the alkene and the thiol, with the aromatic derivatives reacting faster than the aliphatic molecules (73-75). The cooxidation of thiols with 1,3-butadiene was studied in the presence of t-butylamine (76), wherein it was observed that the reaction pathway (1,2-addition versus 1,4-addition to the conjugated dienes) was dependent on the structure of the diene (76-78).

Thiols undergo a facile photolytic reaction to yield the disulfides (79). The primary photolytic process by irradiation at 2500 Å for methanethiols and ethanethiols was the homolysis of the S-H bond to give thiyl radicals and a hydrogen atom (80). The thiyl radicals were detected by flash photolysis (81), as also by uv and esr techniques(82-85).

Radical cations react with thiols to give disulfides, with the intermediate formation of thiyl radicals (86).

The reactions of thiols with dinitrogen tetroxide(87),

seleninic acid (88), selenite (89) and nitrohydroxide ion (90) have been reported. The oxidation of thiol acids by potassium peroxydisulfate (91), and by 2,6-dichlorophenol-indophenol in acetone-water media have been reported (92).

Iron (III) complexes have been used to oxidize thiols to disulfides (93). It was suggested that the disulfide was formed as a result of the dimerization of thiyl radicals(49). Potassium hexacyanoferrate (III) has been used for the oxidation of thiols to disulfides, in alkaline and acid medium (94-98).

PRESENT WORK

The present work is a detailed kinetic investigation of the oxidation of some organic sulfur compounds (thiomalic acid, thioglycolic acid and thiophenol) by potassium hexacyanoferrate (III), in acidic medium, at constant ionic strength, under a nitrogen atmosphere.

Stoichiometry (vide 'Experimental'):

(a) Thiomalic acid

$$2C_4H_5O_4\ SH + 2Fe(CN)_6^{3-} \longrightarrow (C_4H_5O_4)_2\ S_2 + 2Fe(CN)_6^{4-} + 2H^+$$

(b) Thioglycolic acid

$$2C_2H_3O_2SH + 2Fe(CN)_6^{3-} \longrightarrow (C_2H_3O_2)_2\ S_2 + 2Fe(CN)_6^{4-} + 2H^+$$

(c) Thiophenol

$$2C_6H_5SH + 2Fe(CN)_6^{3-} \longrightarrow (C_6H_5)_2\ S_2 + 2Fe(CN)_6^{4-} + 2H^+$$

Effect of substrate and oxidant

The rates of the reactions were observed to be dependent on the first powers of the concentrations of both, substrate and oxidant (Tables 1-3).

Table 1 : Effect of substrate and oxidant

/ Thioglycolic acid / (10^2 x M)	/ $K_3Fe(CN)_6$ / (10^4 x M)	10^5 x k_{obs} (s^{-1})
1.0	15.0	0.7
5.0	15.0	3.6
10.0	15.0	7.2
25.0	15.0	18.2
50.0	15.0	36.8
10.0	2.5	7.2
10.0	7.5	7.3
10.0	10.0	7.2

/HCl/ = 0.1 M; μ = 0.05 M; temp. 35°C.

Table 2: Effect of substrate and oxidant

/Thiomalic acid/ (10^3 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^4 x k_{obs} (s^{-1})
7.5	1.0	14.1
10.0	1.0	19.2
25.0	1.0	46.0
75.0	1.0	140.0
100.0	1.0	192.0
10.0	0.75	19.0
10.0	0.50	19.2
10.0	0.10	19.0

/ HCl / = 0.1 M ; μ = 0.05 M; temp. 35°C

Table 3. Effect of substrate and oxidant

/Thiophenol/ (10^3 x M)	/ $K_3Fe(CN)_6$ / (10^3 x M)	10^5 x k_{obs} (s^{-1})
7.5	1.0	10.0
10.0	1.0	13.7
25.0	1.0	34.0
50.0	1.0	69.0
100.0	1.0	135.0
10.0	0.75	13.8
10.0	0.50	13.5
10.0	0.10	13.8

/ HCl / = 0.1 M; aq. methanol = 80% (v/v);

μ = 5 x 10^{-4} M; temp. 35°C

Plots of k_{obs}, the pseudo first order rate constant, against a 15-fold or a 50-fold range of concentration of substrates, gave straight lines passing through the origin, indicating that the rate of oxidation was dependent on the first power of the concentrations of the substrates. This was further seen by the constant values of k_2, the second order rate constant.

When a constant concentration of substrate(large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant (10-fold range),

indicating a first order dependence of the reaction on the concentration of the oxidant.

Effect of acid

The rate of the reaction was observed to be dependent on the first power of the concentration of acid, in the case of thioglycolic acid and thiophenol (Tables 4-5), but showed an inverse dependence on the concentration of the acid, in the case of thiomalic acid (Table 6).

Table 4. Effect of acid

/ HCl / (M)	$10^5 \times k_{obs}$ (s^{-1}) (Thioglycolic acid)
0.025	1.8
0.05	3.7
0.10	7.2
0.25	18.0
0.50	37.0
0.75	55.0
1.00	75.0

/ Thioglycolic acid / = 0.10 M; / $K_3Fe(CN)_6$ / = 1.5×10^{-3} M; μ = 0.05 M ; temp. 35°C.

Table 5. Effect of acid

/ HCl / (M)	$10^5 \times k_{obs}$ (s^{-1}) at 35°C (Thiophenol)
0.025	3.5
0.05	7.0
0.10	13.7
0.25	34.0
0.50	69.0
0.75	103.0
1.00	140.0

/ Thiophenol / = 0.01 M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3} M; μ = 5 x 10^{-4}M; temp. = 35°C ; aq.methanol = 80%(v/v).

Table 6 : Effect of acid

/ HCl / (M)	$10^4 \times k_{obs}$ (s^{-1}) (Thiomalic acid)
0.075	20.0
0.10	19.2
0.25	12.8
0.50	8.8
1.00	4.0

/ Thiomalic acid / = 0.01 M; / $K_3Fe(CN)_6$ / = 1x10^{-3}M; μ = 0.05 M; temp. 35°C.

An inverse relationship between the rate of the reaction and the concentration of the acid has been observed in earlier investigations such as the oxidation of quinol by ferric ions (99), the cobalt (III) oxidations of formaldehyde (100), tertiary alcohols (101), aromatic aldehydes (102), benzene (103), hydrazoic acid (104-106), the Mn (III) oxidation of quinol (107), and in the oxidation of cysteine and related thiols by hexacyanoferrate (III) ions (108-109).

In the present investigation, the inverse relationship between the rate of the reaction and the concentration of the acid, in the case of thiomalic acid, can be explained if the dissociation step of the sulfhydryl group in the thiol molecule were to be taken into consideration. This, however, appears unlikely, in the acidic medium under consideration. In fact, it is difficult to state with any certainty the extent of involvement of protons vis-a-vis $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions. Ferricyanic acid is a strong acid, but ferrocyanic acid is strong only for the first two protons. The protonation of $Fe(CN)_6^{3-}$ would result in species such as $HFe(CN)_6^{2-}$, while the protonation of $Fe(CN)_6^{4-}$ would give species such as $HFe(CN)_6^{3-}$ and $H_2Fe(CN)_6^{2-}$. These kinds of protonated species have been shown to be formed in acidic media (110).

Nature of the oxidant species

The oxidative power of hexacyanoferrate (III) depends very largely upon its state in solution. At lower acidities of HCl (0.01 M to 0.10 M), the reactive oxidant species was $Fe(CN)_6^{3-}$. At acidities higher than 0.1 M HCl, there is the possibility of the protonation of $Fe(CN)_6^{3-}$ to give $HFe(CN)_6^{2-}$ as the reactive oxidant species.

At lower acidities of HCl (0.01 M to 0.10 M), the absorption maximum of hexacyanoferrate (III) did not show any spectral shift from 420 nm, indicating that $Fe(CN)_6^{3-}$ was not protonated, and hence the reactive oxidant species was $Fe(CN)_6^{3-}$.

At acidities higher than 0.10 M HCl, the absorption maximum of hexacyanoferrate (III) showed a spectral shift from 420 nm to 435 nm, indicating that $Fe(CN)_6^{3-}$ was protonated to give the reactive species as $HFe(CN)_6^{2-}$. The formation of $HFe(CN)_6^{2-}$ was monitored when the absorption spectrum was investigated by varying the wavelength setting, and noting the absorbance about 3 seconds after the reaction had been initiated. In this way, an absorbance maximum was located at 435 nm. A spectral shift from 420 nm to 435 nm would indicate the formation of $HFe(CN)_6^{2-}$. Hence at acidities higher than 0.1 M HCl, the reactive oxidant species was $HFe(CN)_6^{2-}$.

Since the rate of the reaction showed a first order dependence on the concentration of the acid, the first step of the reaction would be the protonation of $Fe(CN)_6^{3-}$ to give $HFe(CN)_6^{2-}$ as the reactive oxidant species, that is,

$$H^+ + Fe(CN)_6^{3-} \underset{}{\overset{K}{\rightleftharpoons}} HFe(CN)_6^{2-} \quad \ldots\ldots \qquad (1)$$

where K was the first protonation constant of $Fe(CN)_6^{3-}$, whose value has been reported (110) to be less than 10. Under the present experimental conditions, the rate law could be expressed as:

$$\text{Rate} = -\frac{d/Fe(CN)_6^{3-}/}{dt} = k_{obs} / \text{Substrate}/ \; /HFe(CN)_6^{2-}/ \qquad \ldots\ldots \qquad (2)$$

$$\text{where } / HFe(CN)_6^{2-} / = K/Fe(CN)_6^{3-}/ \; / H^+ / \ldots\ldots \qquad (3)$$

Effect of temperature

The rate of the reaction was influenced by changes in temperature (Tables 7-9).

Table 7 : Effect of temperature

Temp.($\pm$ 0.1°C)	Thioglycolic acid $10^5 \times k_{obs}$ (s^{-1})
35.0	7.2
40.0	9.9
45.0	13.8
50.0	20.5
55.0	29.7

/ Thioglycolic acid / = 0.10 M; / $K_3Fe(CN)_6$ / = 1.5 x 10^{-3}M; / HCl / = 0.10 M; μ = 0.05 M

Table 8 : Effect of temperature

Temp.($\pm$ 0.1°C)	Thiomalic acid $10^4 \times k_{obs}$ (s^{-1})
25.0	12.2
30.0	16.2
35.0	19.2
40.0	27.2

/ Thiomalic acid / = 0.01 M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; /HCl / = 0.10 M; μ = 0.05 M.

Table 9 : Effect of temperature

Temp ($\pm$ 0.1°C)	Thiophenol $10^5 \times K_{obs}$ (s^{-1})
30.0	10.6
35.0	13.7
40.0	19.3
45.0	25.7
50.0	33.2

/ Thiophenol / = 0.01 M ; / $K_3Fe(CN)_6$ / 1×10^{-3} M;
/ HCl / = 0.10 M; aq.methanol = 80%(v/v);
$\mu = 5 \times 10^{-4}$ M.

Plots of log K_{obs} against the reciprocal of temperature were linear (Figs. 1-3), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies of the reactions (vide 'Experimental': Calculations). The other activation parameters were calculated and have been shown in Table 10 .

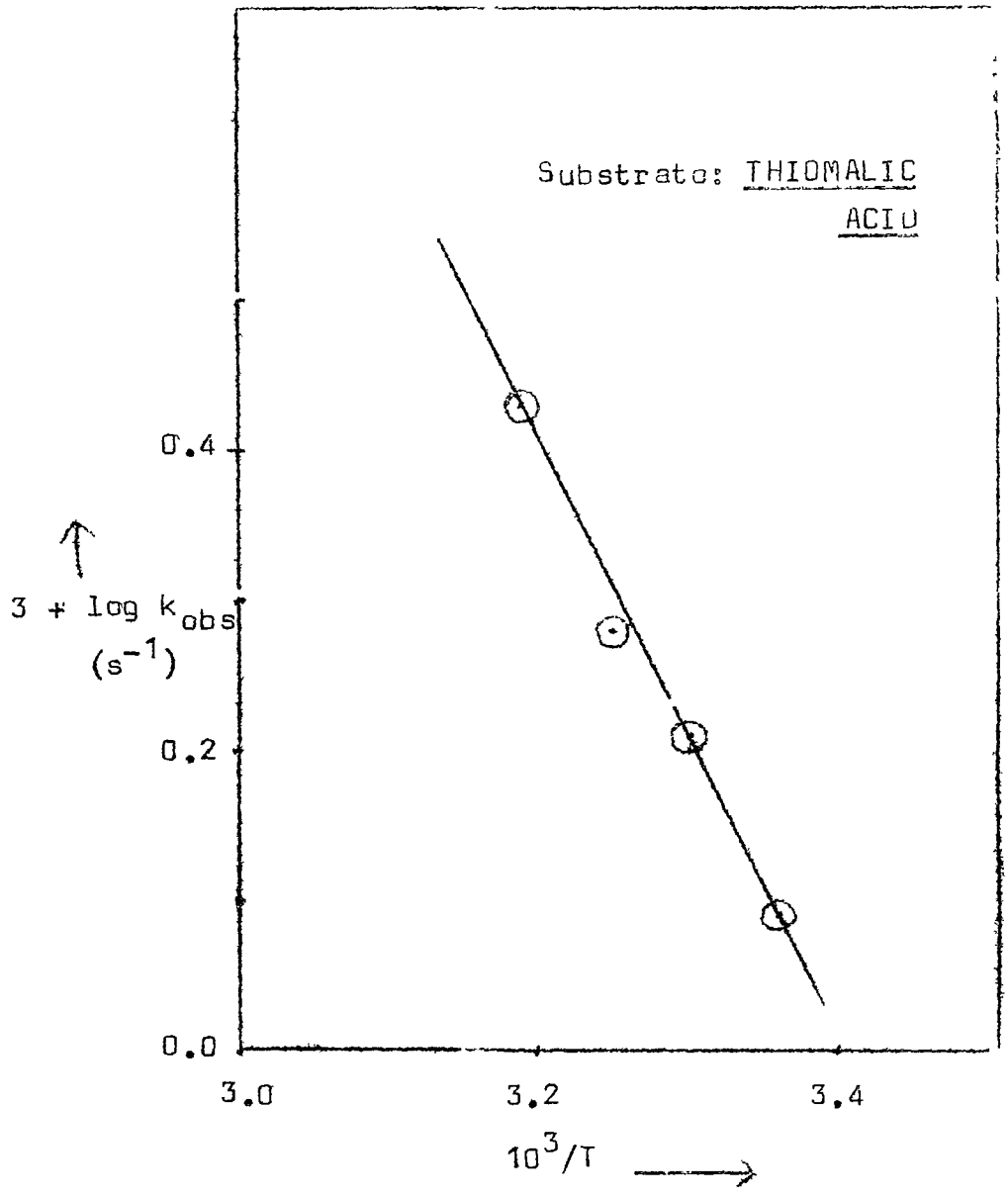

Fig. 1 . Plot of log k_{obs} against the reciprocal of temperature (Substrate : THIOMALIC ACID)

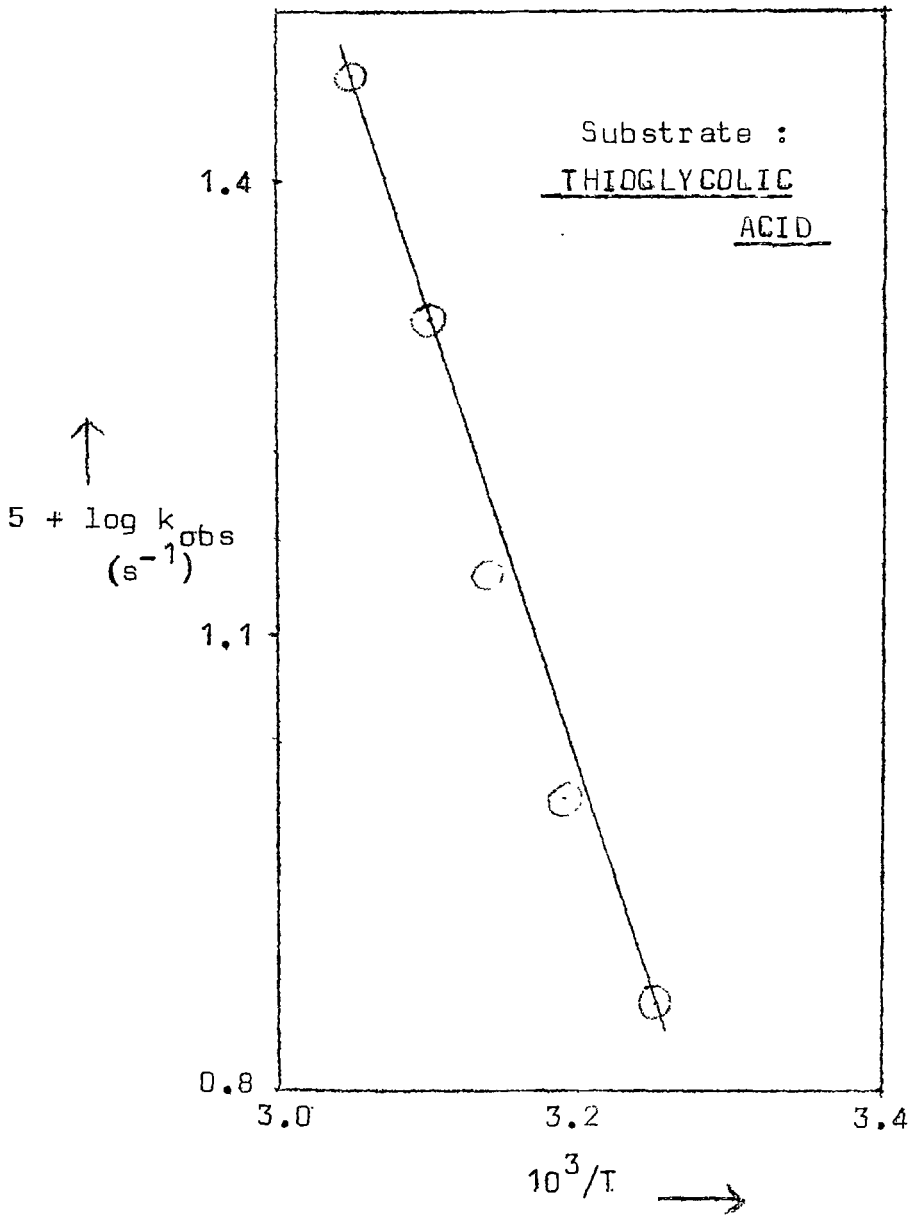

Fig. 2 Plot of log k_{obs} against the reciprocal of temperature

(Substrate: THIOGLYCOLIC ACID)

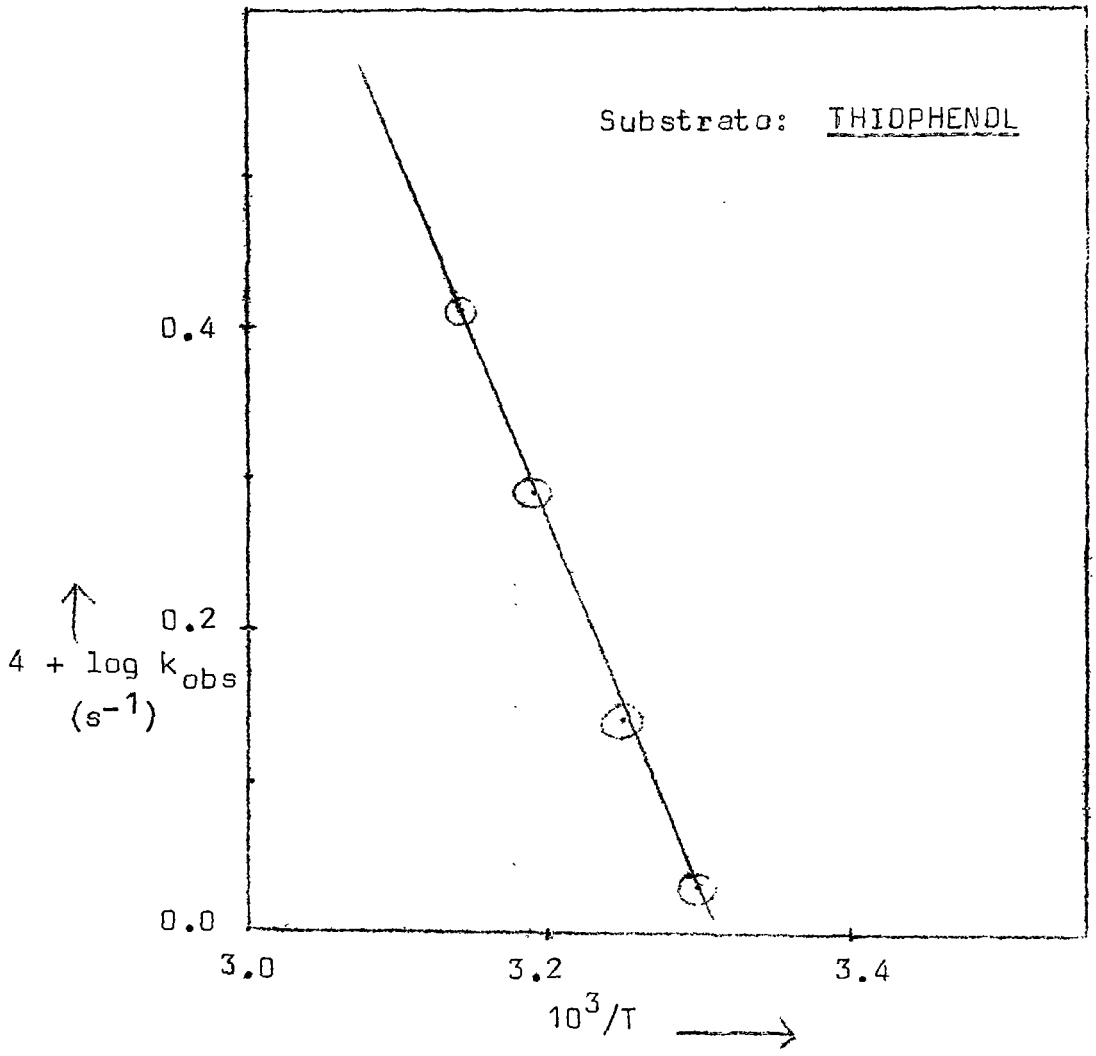

Fig. 3 . Plot of log k_{obs} against the reciprocal of temperature (Substrate : THIOPHENOL)

Table 10 : Activation Parameters

Parameter	Thiomalic acid	Thioglycolic acid	Thiophenol
E(kJ mol^{-1})	40±2	53±3	44±3
A (s^{-1})	$1x10^4$	$9x10^4$	$4x10^4$
$\Delta H^{\neq}$(kJ mol^{-1})	37±2	50±3	41±3
$\Delta S^{\neq}$(JK^{-1} mol^{-1})	-176±5	-160±5	-185±5

The activation parameters are quite favourable for electron transfer processes. If the d orbitals of the sulfur atom are involved in the bonding to the oxidant during the course of the reaction, then the transition state produced will be quite stable. An increase in the bond strength accounts for the large $\Delta S^{\neq}$ value obtained. Values of $\Delta S^{\neq}$ in this range for radical reactions have been ascribed (111) to the nature of the electron-pairing and electron-unpairing processes, and to the loss of degrees of freedom, formerly available to the reactants, on the formation of a rigid transition state. Simple electron transfer reactions leading to the formation of free radicals, and subsequent dimerization of free radicals to give rise to the product, generally exhibit moderately large negative values for the entropy of activation (112).

Effect of solvent

Increasing proportions of methanol resulted in an increase in the rate of the reaction, in the case of thiophenol (Table 11).

Table 11 : Effect of solvent

MeOH-H_2O (%, v/v)	Dielectric Constant(D)	10^5 x k_{obs} (s^{-1})
65-35	48.8	8.0
70-30	46.4	9.6
75-25	44.0	10.7
80 -20	41.6	13.7
85-15	39.2	17.0

/ Thiophenol / = 1 x 10^{-2}M; / $K_3Fe(CN)_6$ / = 1x10^{-3}M;

/ HCl / = 0.1 M; μ = 5x10^{-4} M; temp. = 35°C.

This was due to the lowering of the dielectric constant of the medium, which would favour a less polar transition state compared to more polar reactants.

A plot of log k_{obs} against the reciprocal of the dielectric constant (D) was linear (Fig.4), indicating that the reaction was of the ion-dipole type (113).

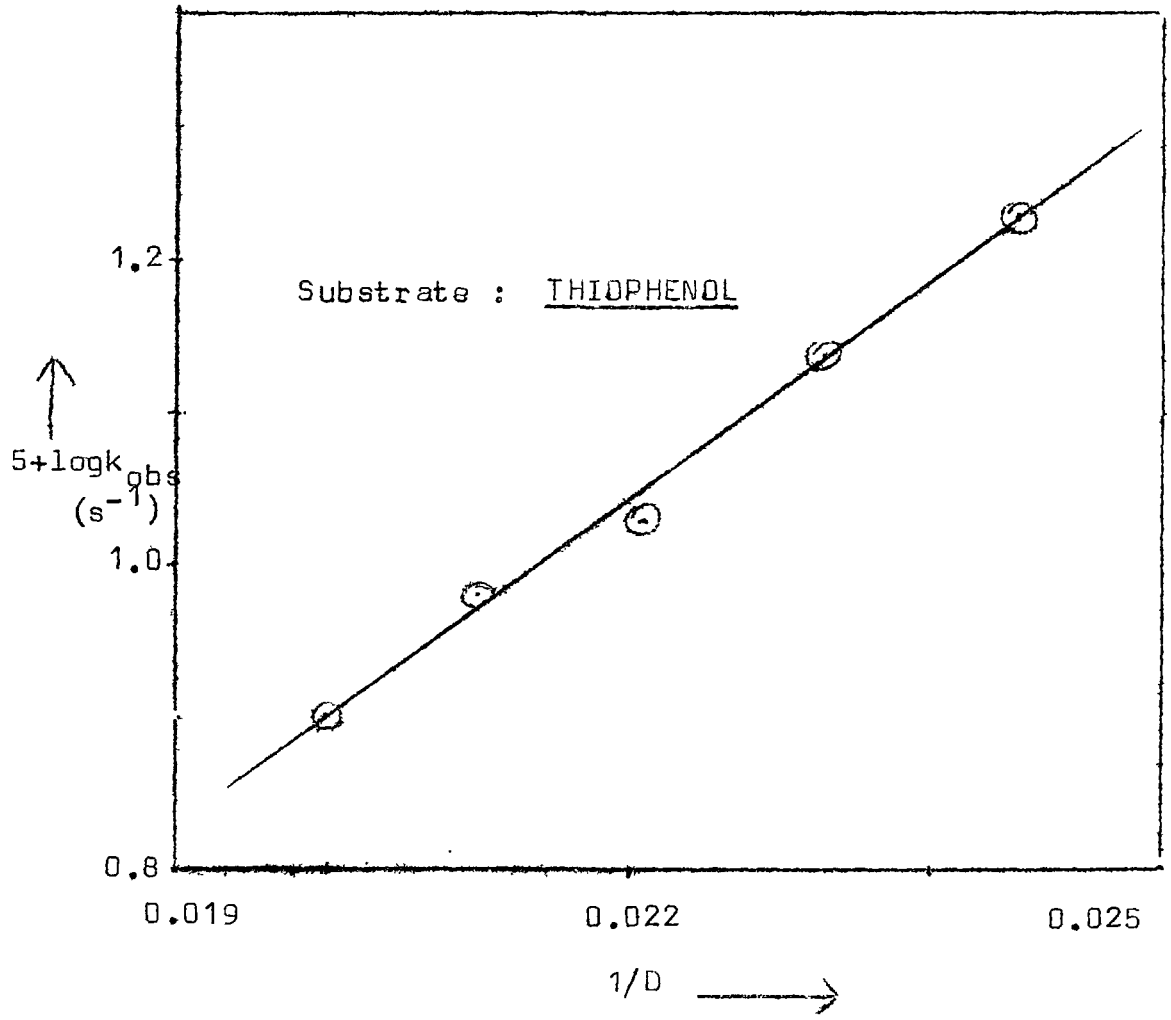

Fig. 4 . Plot of log k_{obs} against the reciprocal of the dielectric constant (Substrate : THIOPHENOL)

The effect of a change in the solvent composition on reaction rates would also depend on factors such as the solvating power of the solvent (114), solute-solvent interactions (115-116), and solvent structure.

Solvent effects on the rates of oxidation of thiols has received considerable attention, wherein the rate increased quite steadily on passing from alcoholic to non-protic and to dipolar aprotic solvents (55-57). A correlation of the rate of oxidation with the pK_a of the alcohol was inferred (55). Large variations in rates were observed, on changing the cation, suggesting that ion-pairing phenomena were involved(55).

Effect of ionic strength

Variations in the ionic strength of the medium using KCl (μ = 0.01 M to μ = 0.10 M for thiomalic acid and thioglycolic acid; μ = 5 x 10^{-4}M to 5x10^{-3} M for thiophenol), did not have any effect on the rates of the reactions.

Effect of added $K_4Fe(CN)_6$

The addition of $K_4Fe(CN)_6$ in the concentration range of 1.0 x 10^{-4} M to 1.0 x 10^{-3}M (for thiomalic acid thiophenol), and in the concentration range of 2.5 x 10^{-4}M to 2.5 x 10^{-3}M (for thioglycolic acid), did not have any effect on the rates of the reactions.

Effect of addition of product

The addition of the product (the respective disulfides, in each case) in the concentration range of 1×10^{-4}M to 1×10^{-3}M, did not have any effect on the rates of the reactions.

Effect of addition of salts

The addition of salts such as NaCl, KNO_3, Na_2SO_4 and $MgSO_4$ (concentration range 0.001 M to 0.01 M) did not have any effect on the rates of the reactions.

Radical intermediates

In the present investigation, the reactions between all the substrates (thioglycolic acid, thiomalic acid and thiophenol) and hexacyanoferrate(III) gave radical intermediates, which was evidenced by the ability of these systems to initiate the polymerization of olefins (117).

The ESR spectra (E-4, Varian) of the radicals generated in a flow system, during the oxidations of each of the substrates with hexacyanoferrate (III), were obtained (vide 'Experimental').

The oxidation of thiomalic acid gave a radical intermediate which showed a 1:2:1 triplet signal, indicating the presence of the thiyl radical.

In the present investigation, the thiyl radicals have been detected and characterized by ESR spectroscopy.

Mechanism

The dimerization of thiyl radicals has been observed to be very fast (138). It has been observed that mercapto radicals generated by flash photolysis in aqueous solutions give rise to a radical ion, possibly by interaction with an ionized thiol molecule (139), that is

$$RS\cdot + R\dot{S}^- \rightleftharpoons RS\dot{S}R \qquad (1)$$

Similar radical anions have been observed (138) as transient species in the reactions of various disulfides with hydrated electrons,

$$RSSR + e^- \rightleftharpoons RS\dot{S}R \qquad (2)$$

which eventually decay to give thiyl radicals and mercaptide ions,

$$RS\dot{S}R \rightleftharpoons RS\cdot + R\dot{S}^- \qquad (3)$$

A related observation was reported (140), wherein a one-electron reduction of naphthalene-1,8-disulfide was postulated, contrary to the more usual two-electron reduction of disulfides (8,10,20,141,142), and also that the radical anion generated from the disulfide with sodium in 1,2-dimethoxyethane has been characterized by ESR spectroscopy (140).

Possible mechanisms for thiol radiolysis in the presence of oxygen have been postulated involving the intermediacy of thiyl radicals (132,133). The reaction

$$RS. + RSSR' \longrightarrow RSSR + R'S.$$

was inhibited by oxygen, the conclusion being that oxygen reacts with the thiyl radical (134).

ESR measurements of radicals produced by the irradiation of cysteine at room temperature have shown that the first step of the reaction involved proton transfer from the radical ion to a neighbouring group, with the formation of the thiyl radical (135). It was suggested that the disulfide was formed as a result of the dimerisation of thiyl radicals.

Thiyl radicals have been observed as the predominant species in the irradiation of alkyl mercaptans (136).

Studies of peptides and proteins containing sulfhydryl and disulfide groups have shown that irradiation at 77 K leads to non-sulfur radicals. On warming, there occurs migration of spins to sulfur, and stable radicals at higher temperatures were observed to be the thiyl radicals (118,122,137).

Thiyl radicals have been detected and characterized in the oxidation of thiols to disulfides, using a variety of oxidizing agents (34,38-41, 47-53).

The oxidation of thioglycolic acid gave a radical intermediate which showed a 1:2:1 triplet signal, indicating the presence of the thiyl radical.

The oxidation of thiophenol gave a radical intermediate which showed a 1:2:1 triplet signal, indicating the presence of the thiophenyl radical ($C_6H_5S\cdot$), which had a value of $g_{av} = 2.027 \pm 0.002$.

The triplet spectrum attributed to RS. radicals was a well-characterized feature of many of the spectra observed in monosulfides and disulfides (118-120). This 'sulfur pattern' was also found in the spectra of various thiols and in compounds containing S-S bonds. A notable feature of many studies of sulfur compounds was the occurrence of striking changes in the structure and size of the absorption peaks as the samples were warmed to room temperature and above (121-123). These effects were quoted as evidence for energy migration in the initial selective fission process, followed by secondary reactions, probably of positive vacancies and negative ions as well as neutral radicals.

Oxidations producing radical intermediates are well known in sulfur systems. The greater stability of these sulfur-containing radicals has been demonstrated by the experimental observation that α-mercaptoacids yield disulfide

as the reaction products. 1 mole of organic substrate reacts with 1 mole of oxidant, indicating the formation of the disulfide. Such reaction products have been identified previously, the oxidation of dithiobiuret by ceric ion giving a cyclic cation as a result of sulfur - sulfur bond formation (124-125).

The presence of thiyl radicals has been shown in earlier investigations. Pulse radiolysis studies showed the presence off a transient species when thiols were irradiated at a pH when some ionization of the thiol group had occurred (126). These species were formed by the reaction of the thiyl radical with the thiolate ion in an equilibrium reaction such as

$$RS\cdot + RS^- \rightleftharpoons RS\overset{-}{S}R$$

In the case of cysteamine, the second order rate constant decreased with an increase in thiol concentration and pH, implying that the rate of disappearance was controlled by the dimerization of free thiyl radicals (126). Similar results were obtained for cysteine (127), mercaptoethanol (128-129), various alkyl mercaptans (128), hydrogen sulfide(130) and penicillamine (131).

It has been shown that oxygen reacts with the thiyl radical according to the reaction

$$RS\cdot + O_2 \longrightarrow RSOO\cdot$$

It could be suggested that disulfide was formed within the coordination sphere of the metal or in a step concerted with the release of the thiyl radical. As in the case of cyanide complexes, it can be assumed that the oxidation of thiols occurred by an outer sphere process, and hence thiyl radicals were formed which would undergo rapid dimerization to yield the disulfide.

It was suggested that the metal catalyzed oxidation of thiols was based on an electron transfer from the metal in its higher oxidation state to the thiol via an inner sphere process whenever the thiol could coordinate to the metal. Outer sphere processes were suggested when strong complexing agents prevented entry of the thiol into the coordination sphere of the metal (66).

The primary photolytic process by the irradiation of thiols at 2500 Å was the homolysis of the S-H bond to give thiyl radicals and H atom (79). The principal products of the reaction were molecular hydrogen and disulfide

$$RSH \xrightarrow{h\nu} RS. + H.$$

$$RSH + H. \longrightarrow RS. + H_2$$

$$2\ RS. \longrightarrow RSSR$$

Thus, in the oxidation of thiols, the main path seems to be the homolytic fission of the S-H bond, leading

to the formation of thiyl radicals, which then undergo rapid dimerization to give the product, disulfide.

(a) Oxidation of thiomalic acid

Thiomalic acid is a weak tribasic acid whose pK_a values have been reported (143) as follows:

pK_1 (COOH) = 3.1; pK_2 (COOH) = 4.94; and pK_3 (SH) = 10.45.

The external addition of the end products, hexacyanoferrate (II) and dithiodimalic acid (the disulfide), did not have any effect on the rate of the reaction, indicating that these end products were not involved in any reversible electron transfer step. It can be assumed that the thiol exists mostly in the ionized form in aqueous medium. Owing to the acidic medium employed in the present study, this would preclude the ionization of the weak sulfhydryl group. Since disulfide was the final product of oxidation, the sulfhydryl group (- SH) provides the site of attack. For convenience, if the species, $\begin{matrix} CH_2COO^- \\ | \\ CH(SH)COO^- \end{matrix}$, is designated as HSR^{2-}, then the proposed mechanism can be written as :

$$Fe(CN)_6^{3-} + HSR^{2-} \xrightarrow[k_{obs}]{\text{Slow}} HFe(CN)_6^{3-} + RS\cdot^{2-}$$

$$RS\cdot^{2-} + \cdot SR^{2-} \longrightarrow {}^{2-}\ RSSR^{2-}$$

which gives

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}\,[Fe(CN)_6^{3-}]\,[RSH] \quad .$$

The formation of the free radical was supported by the polymerization of acrylonitrile (117), and by ESR spectroscopy wherein the thiyl radical appeared as a 1:2:1 triplet (vide 'Radical Intermediates').

The hexacyanoferrate (II) produced during the course of the reaction is shown as the protonated species, $HFe(CN)_6^{3-}$, in agreement with earlier investigations (96,144).

The product of the oxidation of thiomalic acid by hexacyanoferrate (III) in acid medium, was the disulfide, dithiodimalic acid. This product has been isolated and characterized by spectral methods (vide 'Experimental': Product Analysis).

(b) Oxidation of thioglycolic acid

The first and second dissociation constants for thioglycolic acid have been reported (145) as 2.1×10^{-4} and 2.1×10^{-11} at 25°C, respectively. In acid medium, ionized species would be present, according to the equilibrium:

$$HSCH_2COOH \underset{}{\overset{K_1}{\rightleftharpoons}} HSCH_2COO^- \underset{}{\overset{K_2}{\rightleftharpoons}} {}^-SCH_2COO^- \quad .$$

Since the final product of the oxidation of thioglycolic acid by acidic hexacyanoferrate (III) was the disulfide (dithiodiglycolic acid), the sulfhydryl group (-SH) must provide the reaction site. In the mechanism, the species, $^{-}SCH_2COO^{-}$, has been considered to be the reactive species. For convenience,if this reactive species, $^{-}SCH_2COO^{-}$, is designated as RS^{2-} , then the proposed mechanism can be written as:

$$RS^{2-} + Fe(CN)_6^{3-} \xrightarrow{SLOW} RS^{\cdot} + Fe(CN)_6^{4-}$$

$$RS^{\cdot} + Fe(CN)_6^{3-} \xrightarrow{fast} RS^{\pm} + Fe(CN)_6^{4-}$$

$$RS^{\pm} + RS^{2-} \xrightarrow{fast} RSSR^{2-}$$

The formation of the free radical was evidenced by the ability of the system to initiate the polymerization of acrylonitrile (117), and by ESR spectroscopy wherein the thiyl radical appeared as a 1:2:1 triplet (vide 'Radical Intermediates').

The presence of the transient species of the type, $RS^{\pm}$, has been suggested in an earlier investigation (146).

The addition of the products of the oxidation reaction, hexacyanoferrate (II) and dithiodiglycolic acid (the disulfide), did not have any effect on the rate of the reaction, indicating that these end products were not involved in any reversible electron transfer step.

It is also possible that the hydrogen ion may combine with the hexacyanoferrate (II) ion to form ferrocyanic acid, $HFe(CN)_6^{3-}$, according to the equilibrium.

$$H^+ + Fe(CN)_6^{4-} \underset{}{\overset{K'}{\rightleftharpoons}} HFe(CN)_6^{3-} .$$

The equilibrium constant, K' , has been reported (147) to have a value of 5.40×10^{-5}.

The product of the oxidation of thioglycolic acid by acidic hexacyanoferrate (III), was the disulfide, dithiodiglycolic acid. This product has been isolated and characterized (vide 'Experimental' : Product Analysis).

(c) Oxidation of Thiophenol

The rate of the oxidation of thiophenol by acidic hexacyanoferrate (III) was observed to be dependent on the first powers of the concentrations of each species - substrate, oxidant and acid (Tables 3,5). The first order dependence on the concentration of acid indicated that the first step of the reaction was the protonation of $Fe(CN)_6^{3-}$ to give the reactive oxidant species, $HFe(CN)_6^{2-}$. A spectral shift from 420 nm to 435 indicated the presence of $HFe(CN)_6^{2-}$.

Increasing proportions of methanol resulted in an increase in the rate of the reaction (Table 11). A plot of log k_{obs} against the reciprocal of the dielectric constant(D), was linear, suggesting an ion-dipole interaction.

The addition of salts such as NaCl, KNO_3, Na_2SO_4 and $MgSO_4$, did not have any effect on the rate of the reaction. This would suggest that the reaction was between an ion and a neutral (but dipolar) molecule.

The external addition of the end products, hexacyanoferrate (II) and diphenyl disulfide, did not have any effect on the rate of the reaction, suggesting that these end products were not involved in any reversible electron transfer step.

The solvent isotope effect was measured by preparing identically buffered reaction mixtures in water and in 95% D_2O. The ratio of k_{H_2O} / k_{D_2O} observed was 2.25. An estimation of the solvent isotope effect on the reaction between thiophenol and hexacyanoferrate(III) has not been made earlier. It has been suggested previously that the large fractionation factor of 2.32 for the distribution of deuterium between ethanethiol and water favouring the S-H and O-H bonds (148), and the solvent deuterium isotope effect of k_{H_2O} / k_{D_2O} = 2.27 for hemithioacetal formation, in which an S-H was converted to an O-H bond (149), may be accounted for most satisfactorily if bending as well as stretching (and perhaps other frequencies) were to be taken into account (150). In the present investigation, if the reactants were C_6H_5SH and $C_6H_5S.$, then on the basis of a knowledge of the Δpk values for the relevant acids in

going from H_2O to D_2O, the activities of the various ions in these solvents (H_2O and D_2O) could be calculated. Theoretically, this predicted a value of $k_{H_2O} / k_{D_2O} = 2.20$. This would support the formation of the $C_6H_5S.$ species in the rate determining step of the reaction.

It has been suggested that since the dissociation of the lowest triplet excited states of thiophenol was not possible, the breakdown occurred from the lowest excited singlet state following charge neutralization of the parent ion, with S-H cleavage being the only important process (151). In the analogous case of ethanethiol, a similar S-H cleavage was also observed (152). The radiolysis of thiophenol gave an appreciable yield of hydrogen, indicating the dominating role that the sulfhydryl (-SH) group exerts when it is present in a molecule, the significant process being that of hydrogen abstraction from sulfur, resulting in the formation of the thiophenyl radical ($C_6H_5S.$).

In the present investigation, the oxidation of thiophenol by acidic hexacyanoferrate (III) gave a radical intermediate, $C_6H_5S.$, which showed a 1:2:1 triplet signal in the ESR spectrum. This thiophenyl radical had a value of $g_{av} = 2.027 \pm 0.002$.

Earlier investigations had reported the oxidation of thiophenol to diphenyl disulfide by cyclic voltammetry

in DMF solvent (20), DMSO and TMSO(29), diethyl azodicarboxylate in the dark at room temperature (33), iodosobenzene in refluxing dioxan (37), trimethyl sulfoxonium iodide at 100°C in DMF solvent (153), molecular oxygen catalyzed by strong bases(54), molecular oxygen catalyzed by amines (57), tetramethyl-guanidine which acts both as a base and as a dipolar solvent (59), addition of heavy metal salts (62,63), the 2-(2-naphthyl-mercapto)-1-indanyl hydro-peroxide complex with triethylene-diamine (154), and by molecular oxygen catalyzed by anthra-quinone-1-sulfenic acid, t-butyl hydroperoxide and phenyl benzenethiolsulfinate (155).

In the present investigation, the oxidation of thiophenol by acidic hexacyanoferrate (III) yielded the disulfide (diphenyl disulfide) as the product. This product was isolated and characterized by spectral methods (vide 'Experimental': Product Analysis). The mechanism can be represented as follows:

$$H^+ + Fe(CN)_6^{3-} \overset{K}{\rightleftharpoons} HFe(CN)_6^{2-}$$

$$C_6H_5SH + HFe(CN)_6^{2-} \longrightarrow C_6H_5S\cdot + Fe(CN)_6^{4-} + 2H^+$$

$$2\ C_6H_5S\cdot \longrightarrow C_6H_5S\text{-}S\text{-}C_6H_5$$

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RECORD OF

EXPERIMENTAL VALUES

Methyl Amine

$[\text{Methyl Amine}] = 1.0 \times 10^{-2}$ M; $[\text{NaOH}] = 1.0 \times 10^{-1}$ M;
$[K_3Fe(CN)_6] = 5.0 \times 10^{-4}$ M;
O.D. (420 nm) for temperature in ($^{\circ}$C) at

t_m	35°	40°	45°	50°
0	0.146	0.146	0.146	0.146
5	0.143	0.143	0.139	0.134
5.5	0.140	0.140	0.135	0.130
10	0.138	0.136	0.132	0.124
20	0.134	0.125	0.118	0.106

Ethyl amine

$[\text{Ethyl amine}] = 5.0 \times 10^{-2}$ M; $[K_3Fe(CN)_6] = 5.0 \times 10^{-3}$ M;
O.D. (420 nm) for temperature in ($^{\circ}$C) at

tm	35°	40°	45°	50°
0	0.078	0.078	0.078	0.078
10	0.076	0.076	0.076	0.077
130	0.075	0.074	0.073	0.076
190	0.073	0.072	0.072	0.075
260	0.071	0.070	0.071	0.074

Dimethyl Amine

a) $[K_3Fe(CN)_6] = 5.0 \times 10^{-4}$ M; [NaOH] = 1.0×10^{-1} M; temperature = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [Dimethyl Amine] at

t_m	0.005 M	0.01 M	0.05 M
0	0.124	0.124	0.124
5	0.123	0.123	0.119
10	0.120	0.119	0.117
15	0.119	0.117	0.115
20	0.117	0.116	0.114
25.5	0.114	0.115	0.112

b) $[K_3Fe(CN)_6] = 5.0 \times 10^{-4}$ M; [Dimethyl Amine] = 1.0×10^{-2} M; temperature = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [NaOH] at

t_m	0.1 M	0.25 M	0.5 M
0	0.124	0.124	0.124
5	0.123	0.124	0.124
10	0.119	0.123	0.123
15	0.117	0.119	0.121
31	0.115	0.115	0.118

c) $[\text{NaOH}] = 1.0 \times 10^{-1}$ M; [Dimethyl Amine] $= 1.0 \times 10^{-2}$ M; temperature = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0001 M	0.0005 M	0.00075 M
0	0.026	0.124	0.218
5	0.024	0.123	0.213
15	0.022	0.117	0.206
20	0.020	0.116	0.203
25.5	0.018	0.114	0.200

d) $[K_3Fe(CN)_6] = 5.0 \times 10^{-4}$ M; $[\text{NaOH}] = 1.0 \times 10^{-1}$ M; [Dimethyl Amine] $= 1.0 \times 10^{-2}$ M;

O.D. (420 nm) for temperature in ($^{\circ}$C) at

t_m	35°	40°	45°	50°
0	0.124	0.124	0.124	0.124
5	0.123	0.121	0.120	0.119
10	0.119	0.120	0.117	0.115
15	0.117	0.118	0.111	0.111
20	0.116	0.116	0.111	0.106
31	0.115	0.114	0.105	-

Trimethyl Amine

a) $[\text{Trimethyl amine}] = 5.0 \times 10^{-2}$ M; temp. = $(35.0 \pm 0.1)^{\circ}$C.
O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.005 M	0.0025 M	0.001 M	0.0005 M
0	0.586	0.406	0.275	0.144
6	0.574	0.398	0.269	0.141
10.5	0.572	0.396	0.267	0.141
15	0.571	0.395	0.267	0.140
20.5	0.570	0.394	0.267	0.140
35.5	0.566	0.391	0.265	0.140

b) $[K_3Fe(CN)_6] = 5.0 \times 10^{-3}$ M; temp. = $(35.0 \pm 0.1)^{\circ}$C.
O.D. (420 nm) for [Trimethyl amine] at

t_m	0.05 M	0.25 M	0.5 M
0	0.586	0.586	0.586
6	0.574	0.546	0.524
10.5	0.572	0.535	0.486
15	0.571	0.520	0.438
20.5	0.570	0.490	0.421
25	0.568	0.480	0.393
35.5	0.566	0.447	0.331

c) $[K_3Fe(CN)_6] = 5.0 \times 10^{-3}$ M; [Trimethyl amine] $= 5.0 \times 10^{-2}$ M

O.D. (420 nm) for Temperature in (^oC) at

t_m	35^o	40^o	45^o	50^o
0	0.586	0.586	0.586	0.586
6	0.574	0.578	0.558	0.553
10.5	0.572	0.573	-	0.547
15	0.571	0.568	-	0.545
20.5	0.570	0.560	0.553	0.543
30.5	0.570	0.558	0.546	0.543
40	0.566	0.547	0.542	0.533

Diethyl Amine

a) [Diethyl amine] $= 5.0 \times 10^{-2}$ M; temp. = $(35.0 \pm 0.1)^oC$.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.005 M	0.001 M	0.0005 M
0	0.401	0.242	0.164
31.5	0.395	0.238	0.163
68.5	0.389	0.234	0.158
94.5	0.385	0.230	0.149
125.5	0.380	0.225	0.142

b) $[K_3Fe(CN)_6] = 5.0 \times 10^{-3}$ M; temp. = $(35.0 \pm 0.1)^{\circ}C$.

O.D. (420 nm) for [Diethyl amine] at

t_m	0.05 M	0.25 M	0.5 M
0	0.401	0.401	0.401
31.5	0.395	0.359	0.330
68.5	0.389	0.355	0.316
94.5	0.385	0.340	0.299
125.5	0.380	0.323	0.281

c) $[K_3Fe(CN)_6] = 5.0 \times 10^{-3}$M; [Diethylamine] $= 5.0 \times 10^{-2}$ M;

O.D. (420 nm) for Temperature in ($^{\circ}C$) at

t_m	35°	45°	55°
0	0.401	0.401	0.401
31.5	0.395	0.384	0.379
68.5	0.389	0.379	0.337
94.5	0.385	0.374	0.334
125.5	0.380	0.366	0.330
152.5	0.373	0.360	0.325

Triethyl Amine

a) [Triethyl amine] = 5.0×10^{-2} M; temp. = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0005 M	0.001 M	0.005 M
0	0.052	0.061	0.065
6.5	0.045	0.059	0.065
10	0.041	0.055	0.064
15.5	0.037	0.052	0.063
20	0.032	0.050	0.062
25	0.031	0.050	0.062
32	0.028	0.048	0.060
40	0.025	0.043	0.058

b) $[K_3Fe(CN)_6]$ = 5.0×10^{-3} M; temp. = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [Triethyl amine] at

t_m	0.05 M	0.25 M
0	0.065	0.065
6.5	0.065	0.059
10	0.064	0.053
15.5	0.063	0.045
20	0.062	0.031
25	0.062	0.020
32	0.060	0.011
40	0.058	0.008

N,N - Dimethyl Aniline

a) [N,N-Dimethyl Aniline] = 1.0×10^{-2}M; [KCl] = 1.0×10^{-1} M; [NaOH] = 1.0×10^{-2}M; Solvent = [MeOH: H_2O = 60; 40% v/v] temp. = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.001 M	0.00075 M	0.0005 M	0.00025 M
0	0.152	0.101	0.083	0.045
5.5	0.147	0.092	0.072	0.032
10.5	0.141	0.090	0.068	0.031
15.5	0.139	0.085	0.064	0.028
21	0.133	0.083	0.060	0.024
25.5	0.130	0.079	0.059	0.023
30.5	0.128	0.078	0.057	0.020

b) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; $[NaOH] = 1.0 \times 10^{-2}$ M; $[KCl] = 1.0 \times 10^{-1}$ M; Solvent = [MeOH:H_2O=60:40% v/v] temp. = (35.0 ± 0.1)°C.

O.D. (420 nm) for [N,N - Dimethyl Aniline] at

t_m	0.075 M	0.025 M	0.01 M
0	0.152	0.152	0.152
5.5	0.127	0.145	0.147
10.5	0.106	0.140	0.141
15.5	0.097	0.135	0.139
21	0.087		0.133
25.5	0.082	0.123	0.130
30.5	0.078	0.117	0.128
35.5	0.066	0.110	0.125
45	0.060	0.103	0.121
55.5	0.051	0.092	0.116

c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; $[KCl] = 1.0 \times 10^{-1}$ M;
$[$N,N-Dimethyl Aniline$] = 1.0 \times 10^{-2}$M; temp.=(35.0±0.1)°C.
Solvent = [MeOH: H_2O = 60:40% v/v]
O.D. (420 nm) for [NaOH] at

t_m	0.01 M	0.025 M	0.1 M
0	0.152	0.152	0.152
5.5	0.147	-	0.119
10.5	0.141	-	0.089
15.5	0.139	-	0.075
21	0.133	-	0.060
25.5	0.130	0.113	0.050
30.5	0.128	-	0.042
35.5	0.125	0.109	-
45	0.121	-	-
55.5	0.116	0.104	-
67.5	0.112	-	-

d) [N,N-Dimethyl Aniline] = 1.0×10^{-2}M; [KCl] = $1.0 \times 10^{-}$ M; [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [NaOH] = 1.0×10^{-2}M; temp. = $(35.0 \pm 0.1)^{o}$C.

O.D. (420 nm) for solvent [MeOH% v/v] at

t_m	50%	55%	60%
0	0.152	0.152	0.152
5.5	0.137	0.145	0.147
10.5	0.134	0.143	0.141
15.5	0.132	0.140	0.139
21	0.130	0.138	0.133
25.5	0.128	0.135	0.130
30.5	0.125	0.132	0.128
35.5	0.124	0.127	0.125
45	0.118	0.121	0.121

e) [N,N-Dimethyl Aniline] = 1.0×10^{-2}M; [KCl] = 1.0×10^{-1}M; [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [NaOH] = 1.0×10^{-2}M; Solvent = [MeOH : H_2O = 60:40% v/v]

O.D. (420 nm) for temperature in ($^{\circ}$C.) at

t_m	30°	35°	40°	45°
0	0.152	0.152	0.152	0.152
5.5	0.149	0.147	0.146	0.145
10.5	0.145	0.141	0.142	0.140
15.5	0.142	0.139	0.137	0.132
21	0.139	0.133	0.131	0.127
25.5	0.135	0.130	0.126	0.121
30.5	0.133	0.128	0.122	0.117
35.5	0.130	0.125	0.117	0.112
45	0.124	0.121	0.111	0.104
55.5	0.119	0.116	0.105	0.097

N,N-Diethyl Aniline

a) [N,N-Diethyl aniline] = 1.0×10^{-2}M; [KCl] = 1.0×10^{-1}M; [NaOH] = 1.0×10^{-2}M; temp. = $(35.0 \pm 0.1)^{\circ}$C.

Solvent = [MeOH : H_2O = 60:40% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.00025 M	0.0005 M	0.00075 M	0.001M
0	0.020	0.035	0.045	0.060
5.5	0.017	0.031	0.040	0.058
10	0.015	0.030	0.039	0.053
20.5	0.013	0.028	0.038	0.051
25	0.012	0.026	0.036	0.050
36	0.010	0.024	0.035	0.049

b) [N,N-Diethyl Aniline] = 1.0×10^{-2}M; [KCl] = 1.0×10^{-1}M; [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; temp. = $(35.0 \pm 0.1)^{\circ}$C.

Solvent = [MeOH: H_2O = 60:40% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.025M	0.05M	0.1M
0	0.060	0.060	0.060	0.060
5.5	0.058	0.057	0.056	0.050
10	0.053	0.055	0.052	0.045
17	0.052	0.054	0.047	0.040
20.5	0.051	0.053	0.047	0.039
25	0.050	0.051	0.046	0.036
30.5	0.047	0.048	0.044	0.032

c) [N,N-Diethyl aniline] = 1.0×10^{-2}M; [KCl] = 1.0×10^{-1}M
[$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [NaOH] = 1.0×10^{-2} M;
Solvent = [MeOH: H_2O = 60:40% v/v]
O.D. (420 nm) for temperature in (^oC) at

t_m	30^o	35^o	40^o	50^o
0	0.060	0.060	0.060	0.060
5.5	0.056	0.058	0.054	0.053
17	0.053	0.052	0.053	0.052
25	0.051	0.051	0.051	0.050
36	0.050	0.049	0.050	0.049

Benzyl Amine

a) [Benzylamine] = 1.0 M; temp. = $(60.0 \pm 0.1)^oC$.
O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.01 M	0.025 M	0.05 M	0.075 M	0.1 M
0	0.331	0.355	0.379	0.457	0.490
78	0.328	0.347	0.360	0.354	0.355
109	0.326	0.340	0.349	0.320	0.313
139	0.325	0.337	0.341	0.291	0.275
166.5	0.323	0.333	0.328	0.263	0.246
211	0.320	0.328	0.320	0.252	0.235
242	-	0.311	0.311	0.240	0.230

b) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-1}M; [Benzyl amine] = 1.0 M

O.D. (420 nm) for Temperature in (^{o}C) at

t_m	50^{o}	60^{o}	70^{o}
0	0.490	0.490	0.490
78	0.412	0.355	0.275
109	0.384	0.313	0.235
139	0.359	0.275	0.183
166.5	0.338	0.246	0.151
211	0.306	0.231	0.130
242	0.280	0.216	0.115

c) $[K_3Fe(CN)_6]$ = 1.0x10^{-1}M; temp. = (60.0$\pm$0.1)^{o}C.

O.D. (420 nm) for [Benzylamine] at

t_m	1.0 M	1.25 M	1.5 M	2.0 M
0	0.490	0.490	0.490	0.490
78	0.355	0.328	0.350	0.271
109	0.313	0.307	0.228	0.221
139	0.275	0.237	0.189	0.176
166.5	0.246	0.205	0.154	0.147
211	0.215	0.162	0.113	0.115
242	0.184	0.139	0.085	0.080

Diphenyl Amine

a) [Diphenyl amine] = 1.0×10^{-2}M; [NaOH] = 1.0×10^{-1}M; temp. = $(55.0 \pm 0.1)^{\circ}$C.; solvent = [MeOH:H_2O= 70:30% v/v] [KCl] = 1.0×10^{-2} M

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.001 M	0.00075 M	0.0005 M	0.00025 M
0	0.200	0.095	0.087	0.054
10.5	0.189	0.090	0.081	0.051
20.5	0.180	0.086	0.078	0.050
30.5	0.172	0.082	0.076	0.049
40.5	0.162	0.078	0.072	0.047
50	0.154	0.075	0.069	0.043
60	0.149	0.070	0.066	0.040

b) [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [NaOH] = 1.0×10^{-1} M; temp. = $(55.0 \pm 0.1)^{\circ}$C.; Solvent = [MeOH:H_2O = 70:30% v/v] [KCl] = 1.0×10^{-2} M;

O.D. (420 nm) for [Diphenyl amine] at

t_m	0.05 M	0.025M	0.01 M.
0	0.200	0.200	0.200
10.5	0.179	0.184	0.196
20.5	0.167	0.171	0.196
30.5	0.157	0.165	0.190
40.5	0.155	0.160	0.189
50	0.150	0.156	0.186
60	0.145	0.150	0.180

c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [Diphenyl amine] $= 1.0 \times 10^{-2}$M;
[NaOH] $= 1.0 \times 10^{-1}$M; temp. = $(55.0 \pm 0.1)^{\circ}$C.
[KCl] $= 1.0 \times 10^{-2}$ M;
O.D. (420 nm) for solvent [MeOH% v/v] at

t_m	55%	60%	65%	70%
0	0.200	0.200	0.200	0.200
10.5	0.191	0.190	0.191	0.189
20.5	0.186	0.185	0.184	0.180
30.5	0.177	0.178	0.172	0.172
40.5	0.171	0.169	0.164	0.162
50	0.164	0.162	0.160	0.154
60	0.162	0.156	0.155	0.149

d) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [Diphenyl amine] $= 1.0 \times 10^{-2}$M;
[KCl] $= 1.0 \times 10^{-2}$M; Solvent = [MeOH:H_2O= 70:30% v/v]
temp. = $(55.0 \pm 0.1)^{\circ}$C.
O.D. (420 nm) for [NaOH] at

t_m	0.05 M	0.1 M	0.25 M
0	0.200	0.200	0.200
10.5	0.191	0.196	0.181
20.5	0.186	0.196	0.164
30.5	0.179	0.190	0.150
40.5	0.174	0.189	0.140
50	0.165	0.186	0.131
60	0.159	0.180	0.120

e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [Diphenyl amine] $= 1.0 \times 10^{-2}$M; [NaOH] $= 1.0 \times 10^{-1}$M; [KCl] $= 1.0 \times 10^{-2}$ M;

Solvent = [MeOH : H_2O = 70:30% v/v]

O.D. (420 nm) for temperature in (^oC) at

t_m	40^o	45^o	50^o	55^o
0	0.200	0.200	0.200	0.200
10.5	0.196	0.196	0.193	0.189
20.5	0.196	0.193	0.187	0.180
30.5	0.190	0.186	0.178	0.172
40.5	0.189	0.181	0.171	0.162
50	0.186	0.176	0.166	0.154
60	0.180	0.172	0.162	0.149

Sodium Sulfite

a) [Sodium Sulfite] $= 1.0 \times 10^{-2}$M; [NaOH] $= 1.0 \times 10^{-1}$ M; [KCl] $= 5.0 \times 10^{-2}$M; temp. = $(35.0 \pm 0.1)^oC$.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.001 M	0.00075 M	0.0005 M
0	0.205	0.185	0.139
4	0.175	0.155	0.115
8	0.144	0.132	0.100
12	0.115	0.112	0.081
16	0.090	0.095	0.072
20	0.072	0.079	0.060
24	0.058	0.068	0.045

b) [Sodium Sulfite] = 1.0×10^{-2} M; [$K_3Fe(CN)_6$] = 1.0×10^{-3} M; [KCl] = 5.0×10^{-2} M; temp. = (35.0±0.1)°C.

O.D. (420 nm) for [NaOH] at

t_m	0.05 M	0.1 M	0.25 M
0	0.205	0.025	0.205
4	0.181	0.173	0.161
8	0.163	0.144	0.112
12	0.145	0.115	0.073
16	0.131	0.090	0.045
20	0.119	0.072	0.027
24	0.103	0.058	0.017

c) [$K_3Fe(CN)_6$] = 1.0×10^{-3} M; [NaOH] = 1.0×10^{-1} M; [KCl] = 5.0×10^{-2} M; temp. = (35.0±0.1)°C.

O.D. (420 nm) for [Sodium Sulfite] at

t_m	0.0075 M	0.01 M	0.025 M
0	0.205	0.205	0.205
4	0.185	0.171	0.163
8	0.163	0.144	0.094
12	0.137	0.115	0.056
16	0.119	0.090	0.029
20	0.104	0.072	0.013
24	0.089	0.058	0.006

d) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; [Sodium Sulfite] $= 1.0 \times 10^{-2}$ M; [KCl] $= 5.0 \times 10^{-2}$ M; [NaOH] $= 1.0 \times 10^{-1}$ M; O.D. (420 nm) for temperature in (^{o}C) at

t_m	30^{o}	35^{o}	40^{o}	45^{o}
0	0.205	0.205	0.205	0.205
4	0.181	0.173	0.160	0.157
8	0.161	0.144	0.130	0.112
12	0.138	0.115	0.093	0.072
16	0.108	0.090	0.074	0.041
20	0.089	0.072	0.057	0.023
24	0.075	0.058	0.031	0.008

Sodium thiosulfate

a) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; [NaOH] $= 1.0 \times 10^{-1}$ M; [KCl] $= 5.0 \times 10^{-2}$M; temp. = (35.0$\pm$0.1)^{o}C.

O.D. (420 nm) for [Sodium thiosulfate] at

t_m	1 M	0.5 M	0.25 M
0	0.291	0.291	0.291
6	0.268	0.281	0.284
10.5	0.227	0.279	0.280
15.5	0.166	0.274	0.279
21	0.101	0.262	0.277
26	0.049	0.247	0.274
30.5	0.024	0.230	0.272

b) [Sodium thiosulfate] = 5.0×10^{-1}M; [NaOH] = 1.0×10^{-1}M; [KCl] = 5.0×10^{-2}M; temp. = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0025 M	0.001 M	0.00075 M	0.0005 M
0	0.323	0.291	0.259	0.227
6	0.320	0.281	0.252	0.203
10.5	0.316	0.279	0.244	0.195
15.5	0.312	0.274	0.232	0.185
21	0.310	0.262	0.216	0.174
26	0.308	0.247	0.199	0.158
30.5	0.307	0.230	0.181	0.138
36	0.312	0.213	0.161	0.117
40.5	0.304	0.199	0.141	0.099

c) [Sodium thiosulfate] = 5.0×10^{-1}M; [KCl] = 5.0×10^{-2}M; $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; temp. = $(35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [NaOH] at

t_m	0.5 M	0.25 M	0.1 M	0.05 M	0.025 M
0	0.291	0.291	0.291	0.291	0.291
6	0.280	0.277	0.281	0.279	0.288
10.5	0.273	0.274	0.279	0.276	0.284
15.5	0.266	0.266	0.274	0.272	0.282
21	0.240	0.260	0.262	0.272	0.266
26	0.218	0.245	0.247	0.251	0.260
30.5	0.198	0.221	0.230	0.236	0.239
36	0.172	0.198	0.213	0.218	0.227
40.5	0.159	0.177	0.199	0.202	0.209

d) $[K_3Fe(CN)_6] = 1.0x10^{-3}M$; $[NaOH] = 1.0x10^{-1}M$; [Sodium thiosulfate] = $5.0x10^{-1}M$; $[KCl] = 5.0x10^{-2}M$; O.D. (420 nm) for temperature in (^oC) at

t_m	30^o	35^o	40^o	45^o
0	0.291	0.291	0.291	0.291
6	0.287	0.281	0.275	0.254
10.5	0.279	0.279	0.267	0.240
15.5	0.279	0.274	0.250	0.215
21	0.273	0.262	0.227	0.180
26	0.266	0.247	0.200	0.160
30.5	0.258	0.230	0.169	0.119
36	0.250	0.213	0.146	0.061
40.5	0.243	0.199	0.132	0.020

Sodium Dithionite

a) [Sodium dithionite] = $1.0x10^{-3}$ M; $[KCl] = 5.0x10^{-2}M$; $[K_3Fe(CN)_6] = 1.0x10^{-3}$ M; temp. = $(35+0.1)^oC$.
O.D. (420 nm) for [NaOH] at

t_m	0.075 M	0.1 M	0.25 M	0.5 M
0	0.200	0.200	0.200	0.200
5	0.189	0.175	0.180	0.180
10	0.180	0.170	0.169	0.163
15	0.177	0.164	0.162	0.149
20	0.170	0.157	0.153	0.140
25	0.163	0.150	0.138	0.134
30	0.157	0.152	0.132	0.132
35	0.157	0.146	0.132	0.130
40	0.156	0.142	0.128	0.128

b) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; $[KCl] = 5.0 \times 10^{-2}$ M; $[NaOH] = 1.0 \times 10^{-1}$ M; temp. = (35.0±0.1)°C.

O.D. (420 nm) for [Sodium dithionite] at

t_m	0.00075 M	0.001 M	0.0025 M	0.005 M
0	0.200	0.200	0.200	0.200
5	0.186	0.175	0.169	0.130
10	0.182	0.170	0.154	0.099
15	0.176	0.164	0.134	0.066
20	0.178	0.157	0.120	0.054
25	0.175	0.150	0.114	0.040
30	0.173	0.152	0.104	0.027

c) [Sodium dithionite] = 1.0×10^{-3}; [NaOH] 1.0×10^{-1}M; [KCl] = 5.0×10^{-2}M; temp. = (35.0 ± 0.1)°C,

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0005 M	0.00075 M	0.001 M
0	0.120	0.159	0.200
5	0.067	0.120	0.175
10	0.063	0.110	0.170
15	0.059	0.108	0.164
20	0.055	0.103	0.157
25	0.051	0.099	0.150
30	0.048	0.095	0.152

d) [Sodium dithionite] = 1.0 x 10^{-3}M; [NaOH] 1.0x10^{-1}M; [$K_3Fe(CN)_6$] = 1.0x10^{-3} M; [KCl] = 5.0 x 10^{-2} M; O.D. (420 nm) for temperature in (^{o}C) at

t_m	30^{o}	35^{o}	40^{o}
0	0.200	0.200	0.200
5	0.193	0.175	0.158
10	0.186	0.170	0.156
15	0.176	0.164	0.142
20	0.168	0.157	0.135
25	0.162	0.150	0.130
30	0.161	0.152	0.122

Potassium metabisulfite

a) [Potassium metabisulfite] = 7.5 x 10^{-3}M; [NaOH] [KCl] = 5.0 x 10^{-2} M; Temp. = (35.0 ± 0.1)^{o}C

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0·001 M	0·00075 M	0·0005M
[illegible]	0.550	0.470	0.355
3.5	0.465	0.405	0.266
6.5	0.371	0.342	0.185
10	0.292	0.255	0.116
14	0.223	0.152	0.067
18.5	0.158	0.093	0.035
21	0.123	0.068	0.018

b) $[K_3Fe(CN)_6]$ = 1.0×10^{-3} M; [KCl] 5.0×10^{-2} M; [Potassium metabisulfite] = 7.5×10^{-3}M; temp. = $(35.0 \pm 0.1)^{\circ}C$

O.D. (420 nm) for [NaOH] at

t_m	0.05 M	0.1 M	0.25 M	0.5 M
0	0.550	0.550	0.550	0.550
3.5	0.484	0.465	0.377	0.360
6.5	0.404	0.271	0.315	0.205
10	0.290	0.252	0.191	0.091
14	0.187	0.223	0.117	0.030
18.5	0.136	0.158	0.075	0.009

c) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [KCl] 5.0×10^{-2} M [Potassium metabisulfite] = 7.5×10^{-3}M; [NaOH] = 1.0×10^{-1} M

O.D. (420 nm) for Temperature in ($^{\circ}C$) at

t_m	30°	35°	40°	45°
0	0.550	0.550	0.550	0.550
3.5	0.465	0.465	0.421	0.415
6.5	0.408	0.371	0.301	0.266
10	0.345	0.292	0.209	0.150
14	0.284	0.223	0.131	0.088
18.5	0.229	0.158	0.105	0.045
21	0.203	0.123	0.065	0.010

SODIUM THIOCYANATE

a) $[\text{Thiocyanate}] = 2.0$ M; $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M;
$[\text{NaOH}] = 5.0 \times 10^{-1}$M; $[\text{KCl}] = 5.0 \times 10^{-2}$ M;
O.D. (420 nm) for temperature in ($^{\circ}$C) at

t_m	50	60	70
0	0.251	0.251	0.251
5	0.242	0.237	0.225
10	0.231	0.220	0.200
15	0.222	0.205	0.195
20.5	0.211	0.193	0.180
25	0.199	0.186	0.176
30	0.190	0.178	0.172

b) $[\text{Thiocyanate}] = 2.0$ M ; $[\text{NaOH}] = 5.0 \times 10^{-1}$M;
$[\text{KCl}] = 5.0 \times 10^{-2}$M; temperature = $(50 \pm 0.1)^{\circ}$C.
O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.001 M	0.00075 M	0.0005 M	0.00025 M
0	0.251	0.228	0.174	0.110
5	0.242	0.210	0.157	0.098
10	0.231	0.202	0.147	0.088
15	0.222	0.196	0.140	0.083
20.5	0.211	0.184	0.130	0.079
25	0.199	0.173	0.124	0.070
30	0.190	0.167	0.114	0.066

c) $[K_3Fe(CN)_6]$ = 1.0×10^{-3} M; [Thiocyanate] = 2.0 M; [KCl] = 5.0×10^{-2} M; temperature = $(50 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [NaOH] at

t_m	0.25 M	0.5 M	1.0 M
0	0.251	0.251	0.251
5	0.242	0.242	0.229
10	0.239	0.231	0.217
15	0.227	0.222	0.208
20.5	0.223	0.211	0.196
25	0.214	0.199	0.189
30	0.204	0.190	0.184

d) $[K_3Fe(CN)_6]$ = 1.0×10^{-3} M; [NaOH] = 5.0×10^{-1} M; [KCl] = 5.0×10^{-2} M; temperature = $(50 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for [thiocyanate] at

t_m	1.0 M	1.5 M	2.0 M
0	0.259	0.251	0.251
5	0.257	0.246	0.242
10	0.251	0.241	0.231
15	0.244	0.236	0.222
20.5	0.241	0.231	0.211
25	0.238	0.227	0.199
30	0.236	0.222	0.190

Thiomalic Acid

a) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; $[HCl] = 1.0 \times 10^{-1}$ M; $[KCl] = 5.0 \times 10^{-2}$ M; temp. = (35.0 ± 0.1)°C.

O.D. (420 nm) for [Thiomalic acid] at

t_m	0.0075 M	0.01 M	0.025 M
0	0.209	0.209	0.209
5.5	0.098	0.065	0.009
10	0.074	0.044	0.007
15	0.060	0.039	0.006
20	0.055	0.026	0.005
25	0.046	0.025	0.004
30	0.040	0.025	0.004

b) [Thiomalic acid] = 1.0×10^{-2}M; [HCl] = 1.0×10^{-1} M; $[KCl] = 5.0 \times 10^{-2}$ M; temp. = (35.0 ± 0.1)°C.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0075 M	0.0005 M	0.001 M
0	0.154	0.109	0.209
5	0.051	0.039	0.065
10	0.037	0.027	0.044
15	0.032	0.022	0.039
20	0.029	0.017	0.026
25	0.026	0.012	0.025
30	0.022	0.011	0.025

c) $[\text{Thiomalic acid}] = 1.0 \times 10^{-2}$ M; $[\text{KCl}] = 5.0 \times 10^{-2}$ M; $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; temp. $= (35.0 \pm 0.1)^{\circ}$C.

O.D. (420 nm) for $[\text{HCl}]$ at

t_m	0.1	0.25 M	0.50 M
0	0.209	0.209	0.209
5	0.065	0.091	0.110
10	0.044	0.084	0.103
15	0.039	0.080	0.099
20	0.026	0.073	0.092
25	0.025	0.072	0.091
30	0.025	0.068	0.087

d) $[\text{Thiomalic acid}] = 1.0 \times 10^{-2}$M; $[\text{HCl}] = 1.0 \times 10^{-1}$M; $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; $[\text{KCl}] = 5.0 \times 10^{-2}$ M;

O.D. (420 nm) for temperature in ($^{\circ}$C) at

t_m	25°	30°	35°	40°
0	0.209	0.209	0.209	0.209
5	0.094	0.078	0.0655	0.051
10	0.087	0.067	0.044	0.043
15	0.082	0.057	0.039	0.036
20	0.076	0.052	0.026	0.031
25	0.074	0.048	0.025	0.026
20	0.070	0.045	0.020	0.020

Thiophenol

a) $[K_3Fe(CN)_6] = 1.0 \times 10^{-1}$ M; [KCl] 5.0×10^{-4}M; Solvent = [MeOH: H_2O = 80:20% v/v] temp.=(35.0±0.1)°C.

O.D. (420 nm) for [Thiophenol] at

t_m	0.0075 M	0.01 M	0.025 M	0.05 M
0	0.535	0.535	0.535	0.535
6	0.491	0.485	0.485	0.418
16	0.480	0.485	0.447	0.283
25	0.471	0.470	0.375	0.227
30	0.468	0.455	0.339	0.180
35	0.465	0.445	0.291	0.152
45	0.458	0.432	0.286	0.126

b) [Thiophenol] = 1.0×10^{-2} M; [HCl] 1.0×10^{-1} M; [KCl] = 5.0×10^{-4} M; Solvent [$MeOH:H_2O$ = 80:20% v/v] temp. = (35.0 ± 0.1)°C.

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0005 M	0.00075 M	0.001 M
0	0.328	0.350	0.535
6	0.290	0.325	0.485
16	0.260	0.289	0.485
25	0.243	0.272	0.470
30	0.231	0.265	0.458
35	0.227	0.249	0.443
45	0.216	0.223	0.431

c) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [Thiophenol] = 1.0x10^{-2}M; [HCl] = 1.0x10^{-1} M; [KCl] = 5.0 x 10^{-4} M;
temp. = (35.0 ± 0.1)°C.
O.D. (420 nm) for solvent [MeOH:H_2O% v/v] at

t_m	65	70	75	80	85
0	0.535	0.535	0.535	0.535	0.535
6	0.512	0.507	0.505	0.485	0.496
16	0.490	0.490	0.478	0.485	0.458
25	0.481	0.481	0.469	0.470	0.432
30	0.474	0.476	0.458	0.460	0.414
35	0.469	0.461	0.449	0.445	0.402
45	0.458	0.450	0.432	0.429	0.390

d) [Thiophenol] = 1.0 x 10^{-2}M; $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M;
[KCl] 5.0 x 10^{-4}M; temp. = (35.0 ± 0.1)°C.
Solvent = [MeOH: H_2O = 80:20% v/v]
O.D. (420 nm) for [HCl] at

t_m	0.1 M	0.25 M	0.5 M
0	0.535	0.535	0.535
6	0.485	0.463	0.430
16	0.485	0.455	0.416
25	0.470	0.441	0.409
30	0.460	0.434	0.401
35	0.445	0.429	0.395

e) [Thiophenol] = 1.0×10^{-2} M; [$K_3Fe(CN)_6$] = 1.0×10^{-3}M;
[HCl] = 1.0×10^{-1}M; [KCl] = 5.0×10^{-4} M;
Solvent = [MeOH : H_2O = 80:20% v/v]
O.D. (420 nm) for temperature in (^{o}C) at

t_n	30	35	40	45
0	0.535	0.535	0.535	0.535
6	0.501	0.485	0.479	0.462
16	0.491	0.485	0.445	0.431
25	0.471	0.470	0.422	0.398
30	0.460	0.456	0.400	0.370
35	0.441	0.445	0.392	0.355
45	0.430	0.431	0.385	0.331

1. KINETICS OF OXIDATION OF SOME ALIPHATIC AMINES BY ALKALINE HEXACYANOFERRATE (III)

The kinetics of oxidation of some aliphatic amines (methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of these reactions were found to be dependent on the first powers of the concentra tions of both, substrate and oxidant. The rate of the reaction was independent of the concentration of alkali in the range studied, for methylamine and dimethylamine. An alkaline pH was necessary for the facile oxidation of these amines. Though there was no dependence on [alkali] over the pH range studied, the reaction was not independent of pH, in the wider sense.

All the other amines (trimethylamine, ethylamine, diethylamine and triethylamine) underwent facile oxidation by aqueous hexacyanoferrate (III) in neutral medium, that is, without using any alkali.

The effect of changes in temperature on the rates of the reactions has been studied, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium,

changes in the concentrations of added hexacyanoferrate (II) ions, and the addition of salts, did not have any effect on the rates of these reactions.

The presence of radical intermediates, formed in the rate determining step of the reaction, has been detected and characterized by ESR spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of radical intermediates in the rate determining step. The radical underwent further reaction to yield the products. The products formed from the oxidation of methylamine, dimethylamine and trimethylamine were the respective N-acyl derivatives. The products from the oxidation of ethylamine, diethylamine and triethylamine, were the respective dealkylated products. These products were characterized by analytical and spectral methods.

2. KINETICS OF OXIDATION OF SOME AROMATIC AMINES BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of some aromatic amines (aniline and substituted anilines, N-methylaniline, N-ethylaniline, N,N-dimethylaniline, N,N-diethylaniline, benzylamine and substituted benzylamines, diphenylamine and substituted diphenylamines) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen

atmosphere,has been studied.

The rates of these reactions were dependent on the first powers of the concentrations of both, substrate and oxidant. The rate of the reaction was independent of the concentration of alkali in the range studied. An alkaline pH was necessary for the facile oxidation of these amines.

The reactions were influenced by changes in the temperature, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, and the addition of salts, did not have any effect on the rates of these reactions.

Increasing proportions of methanol resulted in an increase in the rate of oxidation, in the case of aniline and diphenylamine. In the case of N,N-dimethylaniline, the reverse trend was observed. Plots of log k_{obs} against the reciprocal of the dielectric constant were linear, indicating that the reactions under consideration were of the ion-dipole type.

The introduction of electron-releasing groups caused an increase in the rate of the reaction, whereas electron-withdrawing groups caused a decrease in the rate of the reaction. Hammett plots of log k_{obs} against σ^+ (or σ) were linear, with the values of $\rho^+ = -1.0$ (anilines), and $\rho = -1.0$ (for diphenylamines and benzylamines). The ρ values for these substrates (anilines, diphenylamines and

benzylamines) were in the range for processes wherein the rate determining step involved the formation of radical intermediates.

The oxidation of benzylamine -α-d_2 exhibited a kinetic isotope effect, with k_H/k_D = 6.3, indicating a cleavage of the C-H bond of the methylene group attached to the aryl ring, resulting in the formation of a radical intermediate in the rate - determining step of the reaction.

The presence of radical intermediates was detected and characterized by ESR spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of a radical intermediate in the rate determining step. The radical was rapidly converted to the products. Efforts to isolate intermediate product(s) were not successful.

The products obtained from the oxidation of the various aromatic amines, were:

(a) azobenzene (80-85%), from the oxidation of aniline;

(b) formanilide (70%) from the oxidation of N-methylaniline;

(c) formanilide (70%) and formaldehyde (10%), from the oxidation of N-ethylaniline;

(d) N-methylformanilide (75%), from the oxidation of N,N-dimethylaniline;

(e) formanilide (70%), acetaldehyde (10%) and formaldehyde (10%),

from the oxidation of N,N-diethylaniline;

(f) tetraphenylhydrazine (80%), from the oxidation of diphenylamine;

(g) benzaldehyde (80%) and ammonia, from the oxidation of benzylamine.

The products formed, in each case, were isolated and characterized by analytical and spectral methods.

3. KINETICS OF OXIDATION OF SOME INORGANIC SULFUR COMPOUNDS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of some inorganic sulfur compounds (sulfite, metabisulfite, dithionite, thiosulfate and thiocyanate) by potassium hexacyanoferrate(III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of the reactions were observed to be dependent on the first powers of the concentrations of each, substrate and oxidant. The rates of the reactions were dependent on the first powers of the concentrations of alkali in the range studied, in the case of sulfite, metabisulfite and dithionite ions. In the case of thiosulfate and thiocyanate ions, the rates were independent of the concentrations of alkali in the range studied.

The rates of the reactions were influenced by changes in temperature, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium, and changes in the concentrations of added hexacyanoferrate (II) ions, did not have any effect on the rates of these reactions.

Radical intermediates were detected in the oxidation reactions of sulfite, dithionite and thiocyanate ions.

The mechanistic pathway envisaged the formation of radical intermediates, in the case of the oxidation of sulfite, dithionite and thiocyanate ions. Rapid dimerization yielded the products, which were isolated and characterized. In the oxidation of thiosulfate, the intermediate anion underwent rapid dimerization to yield the product, which was isolated and characterized.

4. KINETICS OF OXIDATION OF SOME ORGANIC SULFUR COMPOUNDS BY ACIDIC HEXACYANOFERRATE (III).

The kinetics of oxidation of some organic sulfur compounds (thiomalic acid, thioglycolic acid and thiophenol) by potassium hexacyanoferrate (III), in acidic medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of the reactions showed a first order dependence on the concentrations of each, substrate and oxidant. The rates of the reactions showed a first order dependence on the concentration of acid (in the case of thioglycolic acid and thiophenol), but showed an inverse dependence on the concentration of the acid, in the case of thiomalic acid.

The rates of the reactions were enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

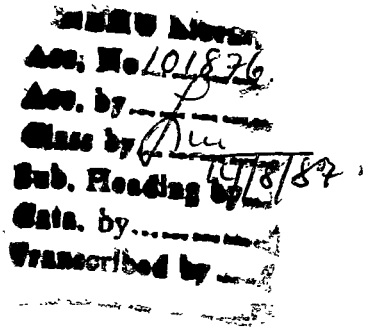
Increasing proportions of methanol resulted in an increase in the rate of the reaction, in the case of thiophenol. A plot of log k_{obs} against the reciprocal of the dielectric constant was linear, indicating that the reaction was of the ion-dipole type.

Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, the addition of salts, and the addition of the product itself, did not have any effect on the rates of these oxidation reactions.

The presence of radical intermediates was detected and characterized by ESR spectroscopy.

The mechanism of the reaction involved the formation

of radical intermediates in the rate determining step. The subsequent step involved a rapid dimerization of the radical, to yield the respective disulfide. The products formed have been characterized by analytical and spectral methods.



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